

THERMODYNAMIC PROPERTIES OF MULTICOMPONENT MIXTURES FROM
THE SOLUTION OF GROUPS APPROACH TO DIRECT
CORRELATION FUNCTION SOLUTION THEORY

By

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To Bonnie, for her support and encouragement
and patience and love

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LIST OF SYMBOLS

$a_{n,\alpha\beta}$	nth order expansion coefficient in perturbation function for pair $\alpha\beta$
$\underline{\underline{C}}$	matrix of direct correlation function integrals
$\underline{\underline{C}}^o$	matrix of short-ranged group direct correlation function integrals
$\underline{\underline{C}}^+$	matrix of purely intermolecular group direct correlation function integrals
c_{ij}	molecular direct correlation function integrals
$c_{\alpha\beta}$	group direct correlation function integral
c_{ij}	molecular direct correlation function
$c_{\alpha\beta}$	group direct correlation function
c_{ijk}	three body direct correlation function integral
$c_{ij}^{\alpha\beta}$	group direct correlation function
f	temperature dependent function
g	temperature dependent function
g_{ij}	pair correlation function
$\underline{\underline{H}}$	matrix of total correlation function integrals
$\underline{\underline{h}}$	supermatrix of group total correlation functions
h_{ij}	total correlation function
$h_{ij}^{\alpha\beta}$	group total correlation function
H^E	excess enthalpy
$\underline{\underline{I}}, \underline{\underline{z}}$	identity matrix and supermatrix
i	molecule

$\underline{\underline{K}}$	matrix of differences between direct correlation function and its angle average
\vec{k}	wave vector
k_B	Boltzmann's constant
M	general property
\overline{M}_α	general partial molar property
N	total number of moles, number of components
N_i	number of moles of species i
O	lowest order
P	pressure
R	gas constant
\vec{R}	position vector
r	distance
\vec{r}	position vector
T	temperature
V, \underline{V}	volume, molar volume
\overline{V}_i	partial molar volume
$\underline{\underline{W}}$	matrix of intramolecular correlation functions
W	intramolecular correlation function integral
$\underline{\underline{X}}$	matrix of mole fractions
$\underline{\underline{X}}$	independent set of mole fractions
X_i	mole fraction of molecule i
Z	compressibility factor
α	generalized hard sphere parameter
β	$= 1/k_B T$, dimensionless inverse temperature
γ_i	activity coefficient
$\delta(\cdot)$	Dirac delta function

δ_{ij}	Kroniker delta
ϵ	energy
η	packing fraction
μ_i	chemical potential
$\underline{\underline{v}}$	matrix of stoichiometric coefficients
ξ_l	lth order packing fraction
ρ	total density
$\underline{\rho}$	vector of densities
$\underline{\underline{\rho}}$	matrix of densities
ρ_i, ρ_α	density of species i or group α
σ_z	supermatrix of intramolecular correlation functions
σ_i	diameter
$\psi_{\alpha\beta}$	perturbation function
Ω	orientation normalization factor
$\underline{\Omega}$	matrix of correlation functions
Ω	correlation function integral
$\underline{\underline{\omega}}, \underline{\omega}$	matrix or supermatrix of intramolecular correlation functions

Subscripts

i, j, \dots	species quantity
n	nth order term in series expansion
α, β, \dots	group quantity

Superscripts

E	excess property
HS	hard sphere property

mix mixture property
o reference state property
PYC, PYV using Percus-Yevick compressibility or virial
forms
r residual property
ref reference
T transpose of a matrix or vector

Special Symbols

- vector
= matrix
~ supermatrix
- partial molar property
< > ensemble average or angle average
^ fourier transform

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A solution of groups technique was developed for use with fluctuation solution theory. The general expressions for calculation of pressure and chemical potential changes from some fixed reference states have been shown. A new corresponding states theory correlation for direct correlation function integrals was proposed and used with the group contribution technique for calculation of pressure changes during compression for several n-alkanes and methanol.

This work gives a detailed analysis of the RISM theory of liquids. Shown are new results for perturbation theory and a generalized compressibility theorem for RISM fluids. The use of the RISM theory for calculation of thermodynamic properties of real fluids also is given.

The use of hard sphere reference fluids for development of equations of state has been explored. A generalized hard sphere equation of state was developed. It was shown that the most accurate hard sphere equation of state is not the best reference system for construction of a liquid phase equation of state of the van der Waals form.

CHAPTER 1 INTRODUCTION

The rational design of chemical process equipment requires knowledge of the thermodynamic properties of the substances involved. More specifically, volumetric properties are needed to size a piece of equipment, enthalpies are needed to determine heat duties, and fugacities are used to decide feasibility of reactions and separations.

The general problem in physical property correlation and estimation is then to determine a procedure for calculation of volumes, enthalpies, and fugacities, for multi-component, multiphase mixtures. This has been accomplished for some pure components using an equation of state with a large number of parameters. Here, a more modest problem is addressed. A formalism is developed that allows the volumetric properties and chemical potentials for liquid mixtures to be expressed in terms of a single group of parameterized functions.

The approach used here tries to recognize the essential differences between liquid and vapor phase properties. A thermodynamically consistent formulation for the volumetric properties and chemical potentials is developed using an equation of state. Here, unlike many other schemes, the

equation of state uses a liquid reference state. This is all made possible by utilization of the Kirkwood-Buff (1951) or fluctuation solution theory.

In an effort to allow for extrapolation of present results to state conditions not examined, the correlations are put into a corresponding states form. This can be justified from analysis of the microscopic theory that is the basis for this macroscopic approach.

Finally, to allow for actual physical property estimation, the theory is cast in a "group-contribution" form. This is easily accomplished formally because the fluctuation solution theory relates molecular physical properties to microscopic correlations. These quantities are well defined for groups, or sites, as they will be often termed.

The next chapter in this work goes into detail in discussing the thermodynamic aspects of the problem and the possible approaches that are available to express the required physical properties. Then, the fluctuation solution theory is outlined.

Chapter 3 is devoted to the discussion of group contribution modeling. Two possible means of linking the group contribution ideas to the fluctuation theory are presented and their differences expounded upon. This chapter concludes with the formulation of the physical property relationships from group correlation function integrals.

Approaches to modeling correlation functions are the emphasis of Chapter 4. General forms, as suggested by

microscopic perturbation theories, are outlined and discussed. The thermodynamic consistency requirements for model formulation are given along with the final expressions for the thermodynamic property changes from the chosen form.

Because the correlation function integrals contain unknown functions, expressed in corresponding states form, some experimental data are required for the model parameterization. In Chapter 5 possible data for this parameterization are discussed critically, and two sets of general correlations are developed. One of these correlations is then decided upon based on the problem of interest and accuracy.

Chapter 6 then presents calculations for several n-alkane molecules' compressions. Both correlations and predictions are shown. Chapter 7 is a general discussion of all of the previously reported work, and Chapter 8 offers several conclusions and recommendations for future work.

There are also several appendices which give greater detail on developments presented in the body and listings of several useful computer programs.

CHAPTER 2 THERMODYNAMIC THEORY

Thermodynamics is a science that has its basis on certain empirical observations that have become known as laws. The simplest of these observations, and the ones most often used in practice, are that mass and energy are conserved quantities. These statements allow for the construction of useful mass and energy balance equations. These balances, when augmented with constitutive relations such as the conditions of phase or reaction equilibria, can be used for design of chemical process units. However, the power of these balance expressions cannot be fully utilized unless the physical properties that appear in the expressions are available.

In the following discussion one other empirical observation is required. This is not known as a law but is often listed as a postulate of thermodynamics (Modell and Reid, 1974). This result may be stated in many ways, but the simplest formulation is as follows: For a simple, homogeneous system of N components, with only P-V work and thermal interactions with its surroundings, that $N+1$ independent, intensive variables are required to specify the state of the system. The simplest use of this observation is the existence of equations of state, such as

$$P = f(T, \underline{V}, \underline{X}) \quad (2-1)$$

Thermodynamic Properties of Interest

As stated previously, this work is concerned with the volumetric properties and chemical potentials of the components in liquid mixtures. The chemical potentials are of interest for phase or chemical equilibrium calculations because of the constraints that are imposed. For equilibrium between phases α and β the constraints are

$$\mu_i^\alpha = \mu_i^\beta v_i \text{ in both } \alpha \text{ and } \beta \quad (2-2)$$

and the chemical equilibrium constraints are

$$\sum_i v_{ij} \mu_i = 0 \quad \forall \text{ reaction } j \quad (2-3)$$

These equilibrium conditions are used to determine both feasible operating conditions for chemical processes and minimum work requirements for some processes.

To size a piece of process equipment one must have knowledge of volumetric properties of the fluids involved. The molar volume of a mixture is found from knowledge of the component partial molar volumes by

$$\underline{V} = \sum_i x_i \bar{V}_i \quad (2-4)$$

An important aspect that must be considered in construction of thermodynamic models is the relationship between chemical potentials and partial molar volumes

$$\left(\frac{\partial \mu_i}{\partial P} \right)_{T, \underline{X}} = \bar{V}_i \quad (2-5)$$

When both the chemical potentials and partial molar volumes are determined from the same equation of state, then equation (2-5) will always be satisfied. However, if different correlations are used for calculating these two different properties, then a thermodynamic inconsistency exists and can cause computational difficulties.

Calculation of Liquid Volumes

Reid, Prausnitz, and Sherwood (1977) give an extensive review of techniques for correlating liquid molar volumes. Most effort has been placed on calculation of saturated liquid volumes because of the insensitivity of liquid volumes to pressure. Most of the correlations are in corresponding states form.

Calculations of compressed (subcooled) liquid volumes often are based on a knowledge of the saturated liquid volume at the system temperature. In general, the volumes are found from expressions of the form

$$\underline{V} = \underline{V}(T, P) \quad (2-6a)$$

$$\underline{V}^{\text{mix}} = \underline{V}(T, P, \underline{X}) \quad (2-6b)$$

These are calculationally convenient forms. If a complete equation of state is used, the volumes are found from solution of the implicit relation

$$P = P(V, T, \underline{X})$$

and care is often necessary to ensure that the proper volume is calculated. Equation 2-1 can be satisfied for several values of the volume at a fixed temperature and composition.

Partial molar volumes are found from the definition

$$\bar{V}_i = \left(\frac{\partial V}{\partial N_i} \right)_{T, P, N_j \neq i} \quad (2-7)$$

For most correlations this is evaluated by using one of the pure component correlations with a set of mixing rules applied to the parameters.

Chemical Potentials and Fugacities

Chemical potentials are used for solution of phase or reaction equilibria problems. However, the chemical potentials themselves are not often used because the equilibrium expressions can be written in terms of the fugacities, defined by

$$\mu_i = \mu_i^0 + RT \ln (\hat{f}_i / f_i^0) \quad (2-8)$$

where the superscript o refers to a given reference state of a specified pressure, composition, and phase at the system temperature, T. The fugacity can be found from two general approaches based on different reference states. For the ideal gas reference state a complete equation of state is required, one that can reasonably predict the system volume. Another, more common, approach is to use a liquid reference state and an expression for the excess Gibbs free energy. In this formulation the fugacity is written as

$$\hat{f}_i = x_i \gamma_i f_i^o \quad (2-9)$$

The γ_i term, known as the activity coefficient, is found from the free energy model and is used to correct for composition nonideality in the liquid solution.

Mathias and O'Connell (1981) have proposed a slight variant on this liquid reference state scheme. Their approach is based on using the temperature and the component densities, $\rho_i = N_i/V$ as the independent variables to describe the state of the system. Then, at constant temperature the following relation holds:

$$d \ln \hat{f}_i = \sum_j \left(\frac{\partial \ln \hat{f}_i}{\partial \rho_j} \right)_{T, \rho_k \neq j} d\rho_j \quad (2-10)$$

Fugacity ratios can be calculated based on any reference state if the partial derivatives in equation 2-10 are known.

Expressions for these derivatives in terms of integrals of microscopic correlation functions are presented in the next section.

Fluctuation Solution Theory

Fluctuation solution theory (Kirkwood and Buff, 1951; O'Connell, 1971, 1982) is a bridge that connects the thermodynamic derivatives to statistical mechanical correlation function integrals. The basic relation of fluctuation theory is

$$\left(\frac{\partial \langle N_i \rangle}{\partial \beta \mu_j} \right)_{T, V, \mu_k \neq j} = \langle N_i N_j \rangle - \langle N_i \rangle \langle N_j \rangle \quad (2-11)$$

where the brackets denote an average over an equilibrium grand canonical ensemble and $\beta = 1/k_B T$. These averages are related to correlation function integrals by

$$\langle N_i N_j \rangle - \delta_{ij} \langle N_i \rangle = \left(\frac{\rho_i \rho_j}{\Omega^2} \right) \int dl d2g_{ij}(l, 2) \quad (2-12)$$

where $\int dl$ is an integration over all phase space coordinates required for molecule 1 and Ω is the normalization constant for the orientation dependence. The function $g_{ij}(l, 2)$ is known as a pair correlation function and is directly related to a two molecule conditional probability density. It is often more convenient to work with the total correlation function, $h_{ij}(l, 2)$, defined by

$$h_{ij}(1,2) = g_{ij}(1,2) - 1 \quad (2-13)$$

Combination of equations 2-12 and 2-13 leads to

$$\left(\frac{\partial \langle N_i \rangle}{\partial \beta \mu_j} \right)_{T,V,\mu_k \neq j} = \delta_{ij} \langle N_i \rangle + \langle N_i \rangle \langle N_j \rangle H_{ij} \quad (2-14)$$

where we have defined

$$H_{ij} = \frac{1}{V^2 \Omega^2} \int d\vec{R} d\vec{\Omega}_1 d\vec{\Omega}_2 h_{ij}(1,2) \quad (2-15)$$

Now because of the translational invariance of an equilibrium ensemble not subject to external fields

$$h_{ij}(1,2) \equiv h_{ij}(\vec{R}_1, \vec{R}_2, \vec{\Omega}_1, \vec{\Omega}_2) = h_{ij}(\vec{R}_1 - \vec{R}_2, \vec{\Omega}_1, \vec{\Omega}_2) \quad (2-16)$$

and thus we can also write

$$H_{ij} = \frac{1}{V\Omega^2} \int d\vec{R} d\vec{\Omega}_1 d\vec{\Omega}_2 h_{ij}(\vec{R}_1, \vec{\Omega}_1, \vec{\Omega}_2) \quad (2-17)$$

To simplify the further analysis we rewrite equation 2-14 using matrix notation as

$$\left(\frac{\partial \langle N_i \rangle}{\partial \beta \mu_j} \right)_{T,V,\mu_k \neq j} = [\underline{\underline{N}} + \underline{\underline{N}} \underline{\underline{H}} \underline{\underline{N}}]_{ij} \quad (2-18)$$

where the elements of the $\underline{\underline{N}}$ and $\underline{\underline{H}}$ matrices are

$$(\underline{\underline{N}})_{ij} = \delta_{ij} \langle N_i \rangle \quad (2-19a)$$

$$(\underline{\underline{H}})_{ij} = H_{ij} \quad (2-19b)$$

To calculate changes in chemical potentials, one is interested in the inverse of equation 2-18

$$\left(\frac{\partial \beta \mu_i}{\partial \langle N_j \rangle} \right)_{T, V, \langle N_k \rangle, k \neq j} = \{ [\underline{\underline{N}} + \underline{\underline{H}} \underline{\underline{N}}]^{-1} \}_{ij} \quad (2-20)$$

This is most easily expressed in terms of integrals of the direct correlation functions, $c_{ij}(1,2)$, introduced by Ornstein and Zernike (1914). These direct correlation functions are defined by

$$h_{ij}(1,2) = c_{ij}(1,2) + \sum_k \frac{\langle N_k \rangle}{V\Omega} \int d^3c_{ik}(1,3)h_{kk}(3,2) \quad (2-21)$$

Because this integral is not of full convolution form, it may seem that it is not possible to relate the fluctuation derivatives to integrals of the direct correlation functions but that is incorrect. Appendix 1 gives the details of the relationship required. Using equations 2-20 and A1-23 we find

$$\left(\frac{\partial \beta \mu_i}{\partial \langle N_j \rangle} \right)_{T, V, \langle N_k \rangle, k \neq j} = [\underline{\underline{N}}^{-1} - \underline{\underline{C}}/V]_{ij} \quad (2-22)$$

and if the independent variables used are the component densities the result is

$$\left(\frac{\partial \beta \mu_i}{\partial \rho_j} \right)_{T, \rho_k \neq j} = [\underline{\underline{\rho}}^{-1} - \underline{\underline{C}}]_{ij} \quad (2-23)$$

If equation 2-23 is combined with equation 2-10 one finds that

$$\left(\frac{\partial \ln \hat{f}_i}{\partial \rho_j} \right)_{T, \rho_k \neq j} = -c_{ij} \quad (2-24)$$

These relations are most useful because they are required to derive the differential equation of state. If the Gibbs-Duhem equation (at constant T) is written as

$$dP\beta = \sum_i \sum_j \rho_i \left(\frac{\partial \beta \mu_i}{\partial \rho_j} \right)_{T, \rho_k \neq j} d\rho_j \quad (2-25)$$

then it is shown that the equation of state can be found through knowledge of the direct correlation function integrals. Combining equations 2-25 and 2-23 yields

$$dP\beta = \sum_j [1 - \sum_i \rho_i c_{ij}] d\rho_j \quad (2-26)$$

A knowledge of the c_{ij} then allows for the calculation of both pressure changes and fugacity ratios relative to any chosen reference state. These results can also be used to determine partial molar volumes of all components in a mixture.

Summary

This chapter has dealt with some of the properties of interest for process design. The relation, required by thermodynamic consistency, between the partial molar volumes and the chemical potentials has been emphasized. Mention was made of the common forms of correlations for these quantities, asserting that often liquid reference state approaches are used for both. The final section presented the fluctuation solution theory that allows for calculation of the partial molar volumes and chemical potentials, based on any reference state, to be expressed simply in terms of one set of functions.

CHAPTER 3 GROUP CONTRIBUTIONS

One of the more powerful tools developed for physical property estimation has been the group contribution concept. The term group normally refers to the organic and inorganic radicals but can be more specific. A molecule of interest can be described by the number of the different types of groups of which it is composed.

There are two general methods for using the group contribution concept. In the first approach some molecular property is written in terms of the state variables and a set of parameters, θ ,

$$M = M(T, P; \theta) \quad (3-1)$$

and the parameters for a given set of substances are found as sums of group contribution

$$\theta_i = \sum_{\substack{\text{all} \\ \text{groups } \alpha}} \theta_{i\alpha} \quad (3-2)$$

The most common forms of this type of formulations have been for predicting critical properties (Lydersen, 1955) and ideal gas specific heats (Verma and Doraiswamy, 1965).

In some cases this technique can be justified on molecular grounds.

The second use of group contribution ideas has been to assume that the groups actually possess thermodynamic properties and that the molecular properties are then a sum of these group properties,

$$\bar{M}_i = \sum_{\substack{\text{all} \\ \text{groups} \\ \alpha \text{ in } i}} \bar{M}_\alpha \quad (3-3)$$

This idea is the basis for two popular activity coefficient correlations, ASOG (Derr and Deal, 1968) and UNIFAC (Fredendslund et al., 1975). A model for the group properties must be developed for this technique to be useful.

The true utility of the group contribution approach stems from its predictive ability. Because all of the molecules in a homologous series are formed of the same groups, only in different proportions, the data for several of the elements of the series can be used to establish the group property correlations. These can then be used to predict the properties of the other series members. This has even greater scope for mixtures.

Consider for example mixtures of n-alkanes and n-alkanols. They can be considered to be made of only three groups, -OH, -CH₂, and -CH₃. Thus, any mixture of the alkanes and alkanols can be described by the concentration of these three groups. If a viable theory exists for some property in terms of the group functions, then

the properties of all mixtures of these groups are set. Figure 3-1 shows an application of these ideas for calculation of the excess enthalpy of alkane-alkanol mixtures. The figure shows the surface of the excess enthalpy for all mixtures of the hydroxyl, methyl, and methylene groups calculated using the UNIFAC equation (Skjold-Jørgensen et al., 1979). Any compound made of the three groups is represented by a point in the base plane. For example, the point ($X_{CH} = 1/2$, $X_{CH} = 0$, $X_{OH} = 1/2$) is that for methanol. The possible group compositions for any mixture are found along the line connecting two molecular points. In the figure these lines are drawn in for methanol-pentane, ethanol-pentane, and pentanol-pentane. The prediction of the excess enthalpy is then found by the intersection of a vertical plane along the composition path and the property surface. To obtain the enthalpy prediction of the molecular system, the ideal solution value must be subtracted from the group estimate. The ideal solution line simply connects the property surface at the points of the pair molecules. The enthalpy prediction for a molecular system of methanol and pentane and at ($X_{ME} = 2/3$, $X_{PE} = 1/3$) is shown as the value H_O^E in the figure. The power here is that this one diagram can be used to find excess enthalpies for all alkane-alkanol mixtures.

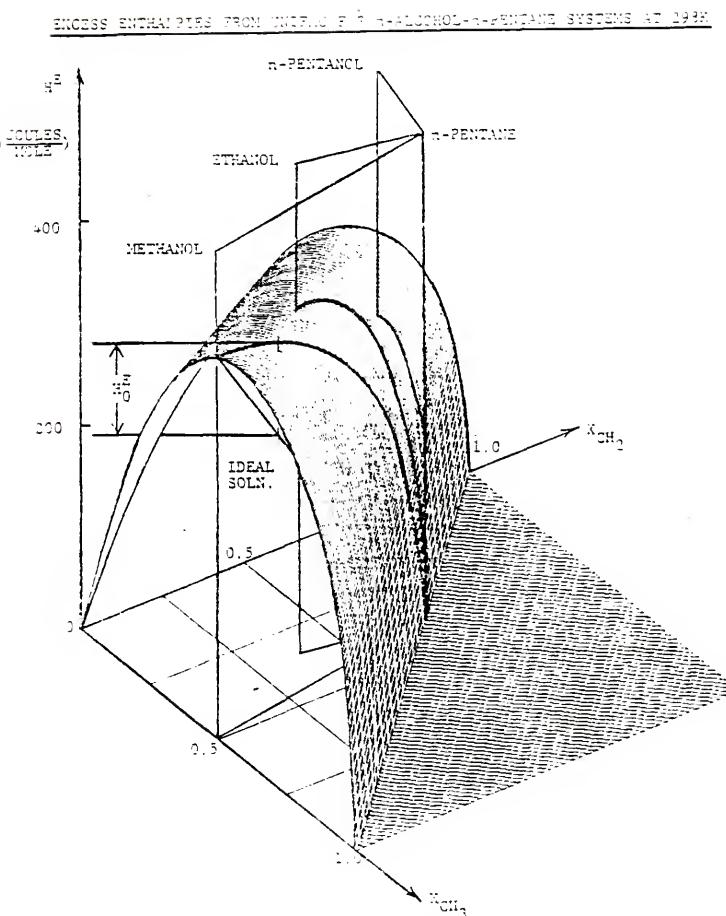


Figure 3-1. Excess enthalpy surface for n-alkane-n-alkanol systems at 298 K calculated using UNIFAC theory.

"Reactive" System Theory

Equation 3-3 can also be written as

$$\bar{M}_i = \sum_{\alpha} v_{i\alpha} \bar{M}_{\alpha} \quad (3-4)$$

where $v_{i\alpha}$, the stoichiometric coefficient, represents the number of groups of type α in molecule i . This expression is completely analogous to that found for a system of groups "reacting" to form the molecule

$$\sum_{\alpha} v_{i\alpha}^{\alpha} \rightarrow i \quad (3-5)$$

With this idea the group contribution expressions have a physical interpretation and the thermodynamics of "reactive" systems (Perry et al., 1981) can be applied to obtain many results.

The motivation here has been to use the fluctuation solution theory in terms of the direct correlation function integrals. It is then desirable to determine the relationship between the molecular and group direct correlation functions. This has been accomplished in a very general fashion by Perry (1980). The development is lengthy, but the salient features are presented below.

The most important aspect of this approach is that even if the groups do not have a thermodynamics, there are still well-defined correlations between groups. This allows for the development of the Kirkwood-Buff theory

in terms of group fluctuation, with the constraints offered by equation 3-5. The result is

$$\left(\frac{\partial \beta \mu_i}{\partial \rho_j} \right)_{T, \rho_k \neq j} = [\underline{\underline{v}}^T (\underline{\underline{\rho}}'^{-1} - \underline{\underline{C}}') \underline{\underline{v}}]_{ij} \quad (3-6)$$

where $\underline{\underline{\rho}}'$ is the matrix of group densities and $\underline{\underline{C}}'$ is a matrix of group direct correlation function integrals.

While this theory is formally exact for the "reactive" system, it can be difficult to apply. The correlation function integrals contain both inter- and intramolecular contributions. For the total correlation functions these effects can be separated, but no known analogous result exists for the direct correlation functions (Lowden and Chandler, 1979). This is a problem that becomes of great importance in attempting to model the correlation function integrals.

RISM Theory

Chandler and Andersen (1973) have formulated a molecular theory for hard sphere molecules known as RISM. The molecules are assumed to be composed of overlapping hard spheres or groups. They show how the molecular Ornstein-Zernike equation 2-18 can be reduced to a group form with explicit separation of the intermolecular and intramolecular correlations. This allows them to define group direct correlation function integrals that have only intermolecular

contributions. The development is detailed but the essential result is

$$c_{ij}(1,2) = \sum_{\alpha} \sum_{\beta} v_{i\alpha} v_{j\beta} C_{\alpha\beta}(\vec{r}_i^{\alpha}, \vec{r}_j^{\beta}) \quad (3-7)$$

Note here that the molecular correlation function has orientation dependence even though the group functions, $c_{\alpha\beta}(\vec{r}_i^{\alpha}, \vec{r}_j^{\beta})$, are written for spherically symmetric interactions. Chandler and Andersen discuss many attributes of these group functions but put no emphasis on the thermodynamic ramifications of these findings.

Differences between RISM Theory and "Reactive" Solution Theory

The major difference between the RISM theory and the "reactive" solution theory is the nature of the direct correlation functions. In Perry's formulation we have

$$c_{\alpha\beta}(\vec{r}_{\alpha\beta}) = \text{direct correlation function between group } \alpha \text{ and group } \beta \quad (3-8)$$

and the RISM theory uses

$$c_{\alpha\beta}(\vec{r}_i^{\alpha}, \vec{r}_j^{\beta}) = \text{direct correlation function between group } \alpha \text{ on molecule } i \text{ and group } \beta \text{ on molecule } j \quad (3-9)$$

This shows that the RISM functions contain less information but may be easier to model because they seem analogous

to molecular functions for which models have been developed. Chandler and Andersen have also presented a variational theory which can be used to obtain the direct correlation functions for hard body systems.

Figure 3-2 shows the results obtained using data from Lowden and Chandler (1973) for a system of hard diatomic molecules. The diatomic molecules are treated as overlapping spheres of diameter σ separated by a distance L . The figure shows that the calculations agree to a reasonable degree with the Monte Carlo calculations for this type of system.

Another important aspect of the Chandler-Andersen theory is that they discuss how the $c_{\alpha\beta}$ functions could be written for real molecules. In general, they show that perturbation theories that would be valid for molecular systems would also apply to RISM group system. The RISM formulation will be employed in the present work.

Thermodynamic Properties from Group Functions

Equations 2-23 and 2-26 can be combined with equation 3-7 to express the molecular thermodynamic differentials in terms of group correlation function integrals. The first quantity required is

$$c_{ij} = \left(\frac{1}{V\Omega^2} \right) \int dld2 c_{ij}(l,2) \quad (3-10)$$

Using equation 3-7 this is

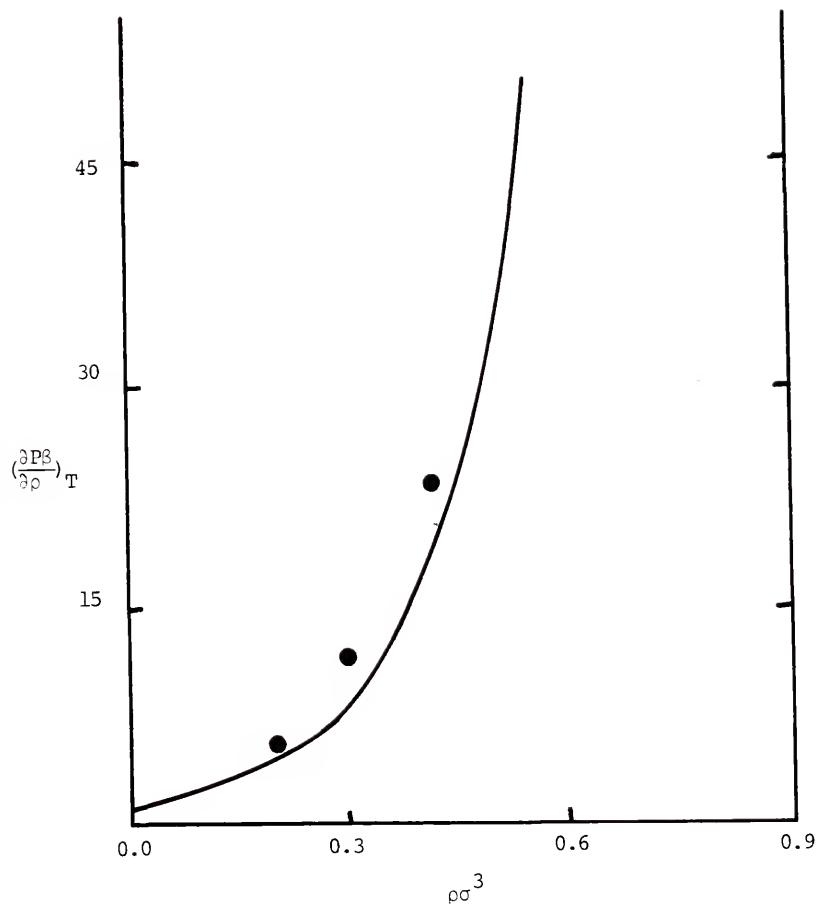


Figure 3.2. Comparison of RISM (----) theory prediction and Monte Carlo (● ●) for a hard, homonuclear diatomic molecule with separation to diameter ratio of 0.6.

$$c_{ij} = \sum_{\alpha} \sum_{\beta} v_{i\alpha} v_{j\beta} \left(\frac{1}{V^2 \Omega^2} \right) \int d\Omega_1 d\Omega_2 c_{\alpha\beta} (\vec{r}_i^\alpha, \vec{r}_j^\beta) \quad (3-11)$$

To evaluate this quantity, a coordinate transformation is required.

$$d\Omega_1 d\Omega_2 = d\vec{R}_1 d\vec{R}_2 d\vec{\Omega}_1, d\vec{\Omega}_2 \rightarrow d\vec{r}_1^\alpha, d\vec{r}_2^\beta d\vec{\Omega}_1 d\vec{\Omega}_2 \quad (3-12)$$

Here, $\vec{\Omega}_i$, represents the set of angles needed to specify the orientation of molecule i with respect to a fixed coordinate system. The above transformation is canonical, and the angular integrations can be performed to yield

$$c_{ij} = \sum_{\alpha} \sum_{\beta} v_{i\alpha} v_{j\beta} \left(\frac{1}{V^2} \right) \int d\vec{r}_i^\alpha d\vec{r}_j^\beta c_{\alpha\beta} (\vec{r}_i^\alpha, \vec{r}_j^\beta) \quad (3-13)$$

Now, the systems under consideration are homogeneous so that

$$c_{\alpha\beta} (\vec{r}_i^\alpha, \vec{r}_j^\beta) = c_{\alpha\beta} (\vec{r}_i^\alpha - \vec{r}_j^\beta) \equiv c_{\alpha\beta} (\vec{r}) \quad (3-14)$$

Then

$$c_{ij} = \sum_{\alpha} \sum_{\beta} v_{i\alpha} v_{j\beta} c_{\alpha\beta} \quad (3-15)$$

where

$$c_{\alpha\beta} = \left(\frac{1}{V} \right) \int d\vec{r} c_{\alpha\beta} (\vec{r}) \quad (3-16)$$

This leads to

$$\left(\frac{\partial \beta \mu_i}{\partial \rho_j}\right)_{T, \rho_k \neq j} = \frac{\delta_{ij}}{\rho_i} - \sum_{\alpha} \sum_{\beta} v_{i\alpha} v_{j\beta} C_{\alpha\beta} \quad (3-17a)$$

or in differential form

$$d\beta \mu_i = \frac{d\rho_i}{\rho_i} - \sum_{\alpha} v_{i\alpha} \left(\sum_{\beta} C_{\alpha\beta} d\rho_{\beta} \right) \quad (3-17b)$$

and the corresponding expression for the pressure variation is

$$dP\beta = d\rho - \sum_a \sum_b \rho_a C_{ab} d\rho_b \quad (3-18)$$

Summary

Group contribution approaches are valuable for predicting thermodynamic properties. In this chapter two general approaches for incorporating group contributions into fluctuation theory have been presented and analyzed. Finally, the thermodynamic property differentials for molecular systems have been expressed in terms of group direct correlation function integrals. Actual property changes can be formulated once models are expressed for the integrals. This is the subject of the next chapter.

CHAPTER 4
FORMULATION OF MODELS FOR
DIRECT CORRELATION FUNCTIONS

In previous chapters it has been shown that changes in thermodynamic properties of molecular systems can be expressed in terms of integrals of site direct correlation function. Expressions for these integrals are required before the calculations can be performed.

The purpose of this chapter is two-fold. First, thermodynamic requirements on models for the direct correlation functions will be presented and examined. With these restrictions on model form established, a feasible model for the correlation function integrals will be presented.

Thermodynamic Consistency

One aspect that has been emphasized throughout this work is the necessity of the formalism to meet thermodynamic consistency requirements. Because our proposed calculational scheme employs direct correlation function integrals, the models that are developed for these quantities are subject to consistency tests. The easiest check that can be employed is one of equality of cross partial derivatives of the (dimensionless) chemical potentials.

$$\left(\frac{\partial^2 \beta \mu_i}{\partial \rho_j \partial \rho_k} \right) = \left(\frac{\partial^2 \beta \mu_i}{\partial \rho_k \partial \rho_j} \right) \quad \forall i, j, k \quad (4-1)$$

This can be expressed in terms of the direct correlation functions integrals because

$$\left(\frac{\partial \beta \mu_i}{\partial \rho_j} \right)_{T, \rho_{k \neq j}} = \frac{\delta_{ij}}{\rho_i} - c_{ij} \quad (4-2)$$

Combination of equations 4-1 and 4-2 leads to

$$\left(\frac{\partial c_{ij}}{\partial \rho_k} \right)_{T, \rho_{l \neq k}} = \left(\frac{\partial c_{ik}}{\partial \rho_j} \right)_{T, \rho_{l \neq j}} \quad (4-3)$$

It must be noted that this is equivalent to the equality of three-body direct correlation function integrals (Brelvi, 1973)

$$c_{ijk} = c_{ikj} \quad (4-4)$$

where the subscripts can take on all values associated with the species in the mixture. The case of interest here is that in which the direct correlation function integrals for the molecular species are written in terms of group quantities

$$c_{ij} = \sum_{\alpha} \sum_{\beta} v_{i\alpha} v_{j\beta} c_{\alpha\beta} \quad (4-5)$$

Then equation 4-3 takes the form

$$\begin{aligned}
 & \left(\frac{\partial}{\partial p_k} \left[\sum_{\alpha} \sum_{\beta} v_{i\alpha} v_{j\beta} C_{\alpha\beta} \right] \right)_{T, p_l \neq k} \\
 &= \left(\frac{\partial}{\partial p_j} \left[\sum_{\alpha} \sum_{\beta} v_{i\alpha} v_{k\beta} C_{\alpha\beta} \right] \right)_{T, p_l \neq j} \quad (4-6)
 \end{aligned}$$

This requirement can be expressed in terms of group properties if the chain rule is used for the derivatives

$$\frac{\partial}{\partial p_i} = \sum_{\gamma} \left(\frac{\partial p_{\gamma}}{\partial p_i} \right) \frac{\partial}{\partial p_{\gamma}} = \sum_{\gamma} v_{i\gamma} \frac{\partial}{\partial p_{\gamma}} \quad (4-7)$$

Combination of equations 4-6 and 4-7 leads to

$$\begin{aligned}
 & \sum_{\alpha} \sum_{\beta} \sum_{\gamma} v_{i\alpha} v_{j\beta} v_{k\gamma} \left(\frac{\partial C_{\alpha\beta}}{\partial p_{\gamma}} \right)_{T, p_{\eta} \neq \gamma} \\
 &= \sum_{\alpha} \sum_{\beta} \sum_{\gamma} v_{i\alpha} v_{k\beta} v_{j\gamma} \left(\frac{\partial C_{\alpha\gamma}}{\partial p_{\beta}} \right)_{T, p_{\eta} \neq \beta} \quad (4-8)
 \end{aligned}$$

This relation will only be satisfied in general if

$$\left(\frac{\partial C_{\alpha\beta}}{\partial p_{\gamma}} \right)_{T, p_{\eta} \neq \gamma} = \left(\frac{\partial C_{\alpha\gamma}}{\partial p_{\beta}} \right)_{T, p_{\eta} \neq \beta} \quad (4-9)$$

Thus, the consistency requirements for group direct correlation function integrals are equivalent to those of the molecular quantities. This constraint will be employed in formulation of the working models for the group direct correlation function integrals.

Basis for Model Development

It has already been shown that the thermodynamic consistency tests for a group formulation and a molecular formulation are equivalent when written in terms of direct correlation function integrals based on the RISM theory. This should not be surprising considering that stability conditions for fluids were shown to be equivalent for the two approaches by Perry (1980). Thus, in developing models for group direct correlation function integrals, the same considerations should apply as those used by Mathias (1979) in developing molecular models.

The general philosophy that will be employed is to use as much theoretical information as possible to develop these models. This requires use of some concepts of statistical mechanical perturbation theory to obtain approximate forms for the correlation function integrals. The analysis of Chandler and Andersen (1972) has shown that for RISM theory direct correlation function results of molecular perturbation theory are easily extended to the group functions. Appendix 2 contains a complete development of an exact perturbation theory for the direct correlation functions based on the RISM theory. In this chapter we shall only deal with the important ramifications of these results.

It is always possible to write

$$C_{\alpha\beta} = C_{\alpha\beta}^{\text{ref}} + (C_{\alpha\beta} - C_{\alpha\beta}^{\text{ref}}) \quad (4-10)$$

where the superscript ref refers to some reference system. The purpose of perturbation theory is to determine a reference system so that an approximate form for the perturbation (second on the right-hand side) term can be made that yields useful results. Because this work is concerned with dense fluids, we require a reference system that can adequately represent the behavior at high densities. In liquids the optimal choice of a reference system seems to be one with only repulsive forces (Weeks, Chandler, and Andersen, 1971). Values of $C_{\alpha\beta}$ are not available for this type of model system. However, the system with purely repulsive forces can be well represented by a system of hard spheres if the hard sphere diameters are chosen as functions of temperature (Barker and Henderson, 1967). This approach will be followed in this work. Even with this choice of reference system the perturbation term cannot be exactly identified. A further approximation used is that the zero density limit of this term is adequate. Thus, the model employed here is

$$C_{\alpha\beta} = C_{\alpha\beta}^{\text{HS}} + \lim_{\rho \rightarrow 0} (C_{\alpha\beta} - C_{\alpha\beta}^{\text{HS}}) \quad (4-11)$$

Appendix 2 shows the evaluation of the required limit which gives the working relation

$$C_{\alpha\beta} = C_{\alpha\beta}^{\text{HS}} + \sum_{n=0}^{\infty} (a_n)_{\alpha\beta} / T^n \quad (4-12)$$

The constants in equation 4-12 are dependent on the intermolecular potential (written as a sum of group of interactions). No explicit calculation of these terms is attempted here because we choose to determine the expressions on the basis of experimental data. This model form is completely analogous to the model used by Mathias (1979).

Analysis of the Model

Several interesting features of the direct correlation function model seem to merit mention. Equation 4-12 is highly similar to the RISM form of the mean spherical approximation (Lebowitz and Percus, 1966; Chandler and Andersen, 1972) and is essentially equivalent if the hard sphere diameters are chosen as functions of temperature only. The assumptions involved in obtaining the present approximant and the mean spherical form are different, but it seems that for our purposes this difference is immaterial.

Of greater interest here is the relationship suggested by the present model for the three-body direct correlation function integrals. These can be found from

$$c_{ijk} = \left(\frac{\partial c_{ij}}{\partial \rho_k} \right)_{T, \rho_l \neq k} \quad (4-13)$$

The form for the c_{ij} proposed in equation 4-12 then suggests that

$$C_{ijk} \approx C_{ijk}^{HS} \quad (4-14)$$

This is probably not a very accurate approximation, but the flexibility in the model form inherent due to the determination of the parameters from experimental data may make this adequate. A better interpretation of this analysis is that the density dependence of the three-body direct correlation function is assumed to be approximated by that of the hard sphere quantity. This analysis also suggests an extension of the RISM theory to three-body correlation functions, a derivation of which can be found in Appendix 3.

$$C_{ijk} = \sum_{\alpha} \sum_{\beta} \sum_{\gamma} v_{i\alpha} v_{j\beta} v_{k\gamma} C_{\alpha\beta\gamma} \quad (4-15)$$

Finally, thermodynamic consistency of the proposed model must be considered. If equation 4-12 is rewritten in explicit form

$$C_{\alpha\beta} (\underline{\rho}, T) = C_{\alpha\beta}^{HS} (\underline{\rho}, T) + \psi_{\alpha\beta} (T) \quad (4-16)$$

then the consistency requirement is met if

$$\left(\frac{\partial C_{\alpha\beta}^{HS}}{\partial \rho_{\gamma}} \right)_{T, \rho_{\eta \neq \gamma}} = \left(\frac{\partial C_{\alpha\beta}^{HS}}{\partial \rho_{\beta}} \right)_{T, \rho_{\eta \neq \beta}} \quad (4-17)$$

In this work, the $C_{\alpha\beta}^{HS}$ are determined from the generalized hard sphere equation of state, which is consistent, then

this must be true. Note that if terms of higher order in density had been included in the perturbation term, they also would have to have been chosen to be thermodynamically consistent.

Also of interest here is the functional dependence of the hard sphere diameters. If they are chosen to be functions of density, as is normally done in the Weeks-Chandler-Andersen perturbation scheme, then this dependence would have to be such that equation 4-17 was satisfied. This is an aspect not always appreciated.

Property Changes Using the Proposed Model

This chapter has presented and analyzed a feasible model for group direct correlation function integrals. The utility of this model can only be tested by its use to calculate changes in molecular thermodynamic properties. The required formulas are developed below.

Chemical Potential

Equation 3-17b expresses the differential of a molecular chemical potential in terms of the group direct correlation function integrals. This is conveniently rewritten in terms of the residual chemical potential as

$$d\beta\mu_i^r = \sum_{\alpha} \sum_{\beta} v_{i\alpha} C_{\alpha\beta} d\rho_{\beta} \quad (4-18)$$

Insertion of equation 4-16 and integration leads to

$$\Delta\beta\mu_i^r = \sum_{\alpha} v_{i\alpha} [\Delta\beta\mu_{\alpha}^{r, HS} + \sum_{\beta} \psi_{\alpha\beta} \Delta\rho_{\beta}] \quad (4-19)$$

where $\mu_{\alpha}^{r, HS}$ is the residual chemical potential calculated from the hard sphere equations for group α in a solution of groups.

Pressure Change

To calculate pressure changes, it is again easiest to work with residual properties. The required differential form is

$$dP_{\beta}^r = - \sum_{\alpha} \sum_{\beta} \rho_{\alpha} C_{\alpha\beta} d\rho_{\beta} \quad (4-20)$$

Insertion of the model and integration leads to

$$\Delta P_{\beta}^r = \Delta P_{\beta}^{r, HS} + (\frac{1}{2}) \sum_{\alpha} \sum_{\beta} \psi_{\alpha\beta} \Delta(\rho_{\alpha}\rho_{\beta}) \quad (4-21)$$

where $\Delta P_{\beta}^{r, HS}$ is the change in the residual pressure (divided by $k_B T$) calculated from the hard sphere equation for the solution of groups.

It should be noted that the ideal gas state used for the residual property changes on either side of equation 4-21 are different. This should be expected for the group equation of state is written in terms of the group densities which sum to a larger value than the molecular densities. However, because this form is not used as a complete equation of state, this should not present a problem.

CHAPTER 5 MODEL PARAMETERIZATION

This work has been concerned with formulating the thermodynamic properties of molecular systems in terms of integrals of group direct correlation functions. In the last chapter a form for these terms was developed

$$C_{\alpha\beta} = C_{\alpha\beta}^{\text{REF}} + \psi_{\alpha\beta} \quad (5-1)$$

and further, the reference state was identified as that of a hard sphere system. The full dependence on state variables is written as

$$C_{\alpha\beta} (\underline{\rho}, T) = C_{\alpha\beta}^{\text{HS}} (\underline{\rho}, T; \underline{\sigma}) + \psi_{\alpha\beta} (1/T) \quad (5-2)$$

where $\underline{\sigma}$ is the vector of hard sphere diameters for the groups in the system. The purpose of this chapter is to develop empirical forms for the functions $\psi_{\alpha\beta}$ and to establish the dependence of the hard sphere diameters on state parameters (Weeks, Chandler, and Andersen, 1971).

Corresponding States Theory

The utility of the form proposed in equation 5-2 can be enhanced if the perturbation functions and hard sphere diameters could be written in corresponding states form. This is a two-step process:

1. Determine if a corresponding states principle exists for the direct correlation function integrals for liquids.
2. Determine if the functional form proposed in equation 5-2 can represent the observed correspondence.

To answer these questions simple molecules will be considered first. The molecules considered here can be considered to consist of only one group. The relation to thermodynamics used in the analysis is

$$\left(\frac{\partial \rho}{\partial P\beta}\right)_T = 1/(1-\rho C) \quad (5-3)$$

Figure 5-1 shows a corresponding states correlation for the quantity on the left-hand side of equation 5-3 for simple molecules, using only one parameter. Further, Brelvi and O'Connell (1972) showed that this behavior can be found for polyatomic molecules also, if the density is large enough ($\rho > 2\rho_C$). These results suggest that for large densities a one-parameter corresponding states formulation may be valid for the direct correlation function integrals.

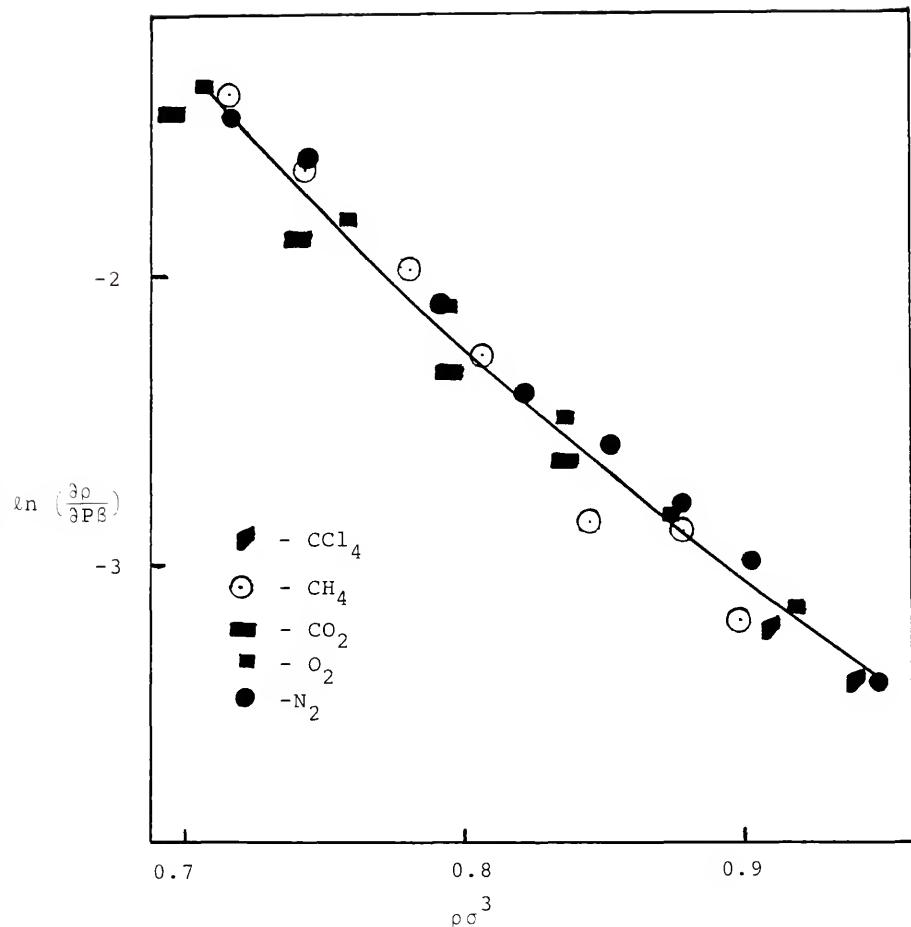


Figure 5-1. Bulk modulus versus reduced density for simple fluids. The line is argon data and σ is Lennard-Jones potential parameter.

Note that the temperature dependence seems to have little effect. Inclusion of temperature dependence in these correlations should be able to enhance the accuracy.

Figure 5-2 shows another test of this correspondence. This is in an integrated form of equation 5-3.

$$p_{\beta} = p_{\beta}^{\text{ref}} + \int_{\rho_{\text{ref}}}^{\rho} (1-\rho C) d\rho \quad (5-4)$$

Here, a characteristic volume for each molecule, V^* , and a characteristic temperature, T^* , have been found to yield the correspondence as

$$\tilde{p} = \tilde{p}^{\text{ref}} + f(\tilde{\rho}, \tilde{T}; \tilde{\rho}^{\text{ref}}) \quad (5-5)$$

where

$$\tilde{p} = PV^*/RT$$

$$\tilde{\rho} = \rho V^*$$

$$\tilde{T} = T/T^*$$

The function, f , in equation 5-5 is a corresponding states correlation for the density integral of the direct correlation function. This is what is desired. The data presented seem to suggest that a corresponding states formulation can be found for pure component direct correlation function integrals for dense fluids. A detailed discussion

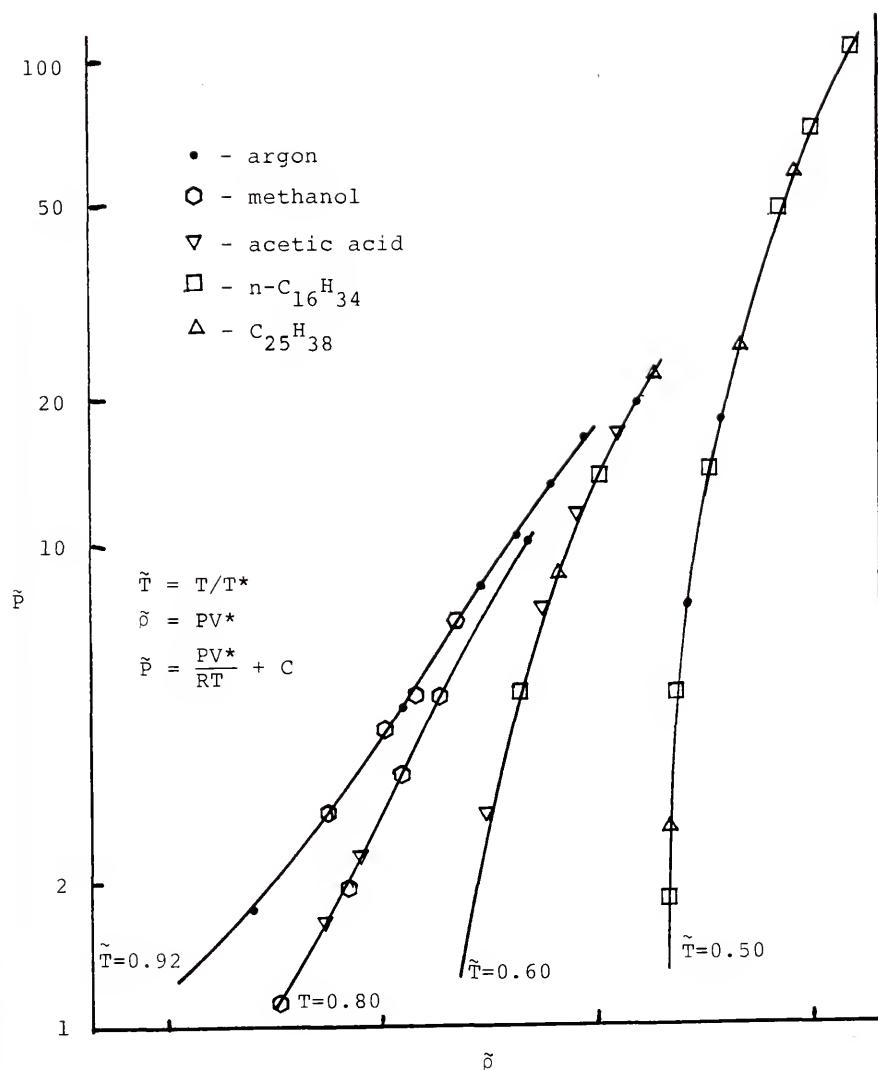


Figure 5-2. Corresponding states correlation for liquids.

of the origins of this correlation is presented in Appendix 4.

Mathias (1979) has shown that these concepts can be extended to mixture-direct correlation function integrals with the proper choice of mixing rules. He used a form similar to equation 5-2, but the group contribution concept was not employed.

The applicability of the two-parameter corresponding states principle seems valid for the direct correlation function integrals. The question of the use of the functional form must now be addressed. This is again most easily accomplished by analysis of a set of experimental data for a simple molecule. After the noble gases are used for this type of testing, however, the major interest here is for hydrocarbons so that a hydrocarbon reference system may prove to be more useful.

Choice of a Reference Component

Mathias (1979) had great success in developing a corresponding states correlation for direct correlation function integrals, using a form similar to equation 5-2, for molecular systems, using argon as a reference component to determine model parameters. This work is concerned with hydrocarbon properties so that it seems reasonable to examine the difference in direct correlation function integrals between argon and a simple hydrocarbon, methane.

The comparison is performed here using the dimensionless quantity $1-\rho C$. Table 5-1 shows this comparison for two isotherms, in the dense fluid region.

The behavior is similar on both isotherms. It is seen that the fluids act quite similarly at lower densities but behave differently as the density becomes larger. Methane is increasingly more compressible as the density increases. This can be explained by the polyatomicity of methane. Both molecules are essentially spherical, but at the higher densities the methane seems to allow for interlocking of the hydrogens.

These effects can be important for the development of the group contribution correlations. If the groups were chosen as monatomic, then argon would probably be the better choice of reference substance due to physical similarity. However, if the groups are chosen as the common organic radicals, then methane may be the better choice of reference substance.

The actual choice of a reference substance will be made after it has been determined whether equation 5-2 is a viable functional form for the direct correlation function integrals.

Method of Data Analysis

This section addresses the question of whether the form proposed in equation 5-2 can be used to fit the direct

TABLE 5-1

COMPARISON OF DIRECT CORRELATION FUNCTION INTEGRALS
FOR ARGON AND METHANE

$T/T_c = 0.76$			$T/T_c = 2.0$		
ρV_c	$(1-\rho C)_{\text{argon}}$	$(1-\rho C)_{\text{methane}}$	ρV_c	$(1-\rho C)_{\text{argon}}$	$(1-\rho C)_{\text{methane}}$
2.26	6.44	6.35	2.1	7.23	7.14
2.31	7.97	7.82	2.2	8.50	8.35
2.37	9.68	9.44	2.3	9.96	9.73
2.43	11.51	11.25	2.4	11.65	11.29
2.48	13.57	13.24	2.5	13.58	13.07
2.54	15.83	15.43	2.6	15.79	15.06
2.59	18.30	17.83	2.7	18.29	17.30
2.65	21.05	20.46	2.8	21.13	19.91
2.70	23.88	23.33	2.9	24.33	22.59
2.76	27.10	26.45	3.0	27.94	25.68

correlation function integrals of real fluids. The analysis will be performed in terms of the dimensionless quantity, C , defined by

$$\bar{C} \equiv \rho C = 1 - \left(\frac{\partial P\psi}{\partial \rho} \right)_T \quad (5-6)$$

The thermodynamic derivative is evaluated from correlated experimental data. From equation (5-2) this is

$$\bar{C} = \bar{C}^{HS}(\rho, T; \sigma) + \rho\psi \quad (5-7)$$

For this work the hard sphere diameter is treated as a function only of temperature. Thus, along an isotherm, if the proposed functional form is proper, for the proper choice of hard sphere diameter, the value of ψ should be constant given by

$$\psi = (\bar{C}^{HS} - \bar{C})/\rho \quad (5-8)$$

for any value of ρ . The suitability of the proposed model is determined by how well this is obeyed. The hard sphere properties are determined using the generalized hard sphere expressions as presented in Appendix 5. It should be noted that all of the hard sphere equations are generated by the same microscopic form of the direct correlation function. Here the hard sphere direct correlation function

integrals are found using equation 5-6 with the corresponding form of the hard sphere equation of state. For these pure component cases we have

$$\bar{C}^{\text{HS}} = \frac{(1+\alpha)\eta^4 - 4(1+\alpha)\eta^3 + 2\eta^2 - 8}{(1-\eta)^4} \quad (5-9)$$

where $\eta = \pi/6 \rho \sigma^3$

and in corresponding states form

$$\eta = [\pi/6 \sigma^3/V^*] [\rho V^*] \quad (5-10a)$$

$$\equiv X \rho V^* = X \tilde{\rho} \quad (5-10b)$$

Here, the characteristic volume, V^* , has been introduced as a reducing parameter for both the hard sphere volume and the density. On each isotherm there are actually two parameters that can be used to vary the model, α and X . The analysis here has been done sequentially, a value of α is chosen and then the optimum X has been found for that value of α . The characteristic volume has also been used to reduce the perturbation term ψ as

$$\psi = (\psi/V^*)V^* = V^*f(T) \quad (5-11)$$

The model can then be written as

$$\bar{C}(\rho, T) = \bar{C}^{\text{HS}}(n; T, X, \alpha) + \beta f \quad (5-12)$$

Figure 5-3 gives a simplified flowchart of how the calculations are performed for each isotherm for a fixed value of α . The subscript i denotes the number of data points on the isotherm, NP . The optimization routine, RQUADD, can be found in Appendix 6.

Analysis of Argon Data

The values of $(\frac{\partial P}{\partial \rho})_T$ needed for this analysis were generated

from the equation of state of Twu et al. (1980). These authors claim to be able to reproduce dense fluid pressures to within the experimental accuracy. Eleven temperatures, evenly spaced between the triple and critical points, were chosen to generate liquid phase data. Each isotherm consisted of 16 density-correlation function integral pairs evenly spaced between the vaporizing and freezing densities. Supercritical data were also used. The isotherms were for values of T/T_c from 1.1 to 3.0. The densities used were in 0.1 increments of ρ/ρ_c from 1.5 to 3.0, or the freezing density, whichever was lower. A listing of the program used to generate the data is given in Appendix 6.

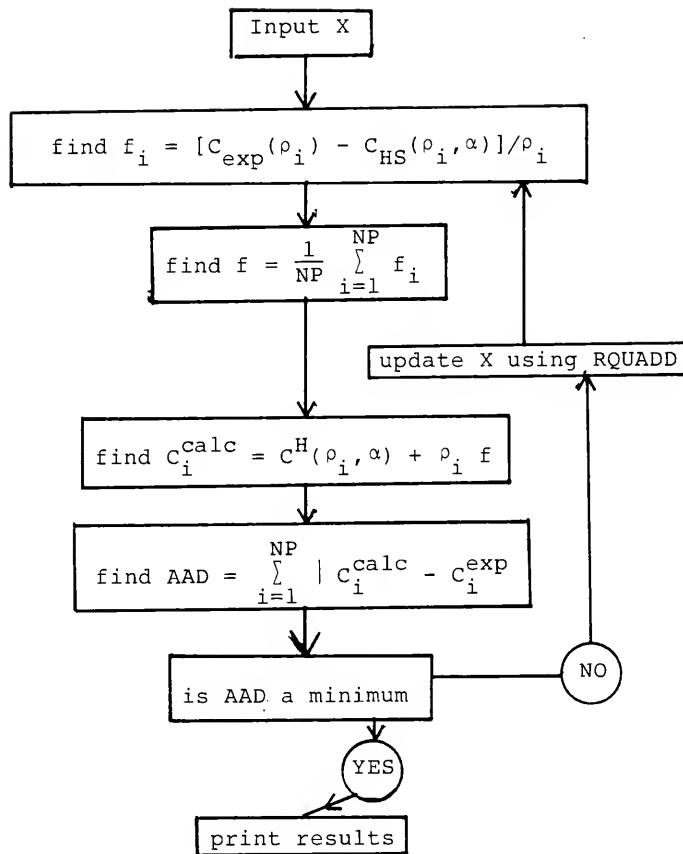


Figure 5-3. Flowchart for calculation of X at a fixed α .

For the initial analysis values of α of 0, -1, -2, -3, -4, and -5 were used. Table 5-2 shows the average absolute deviation in the direct correlation function integrals found for the optimum value of χ at each isotherm. A noticeable minimum exists in the range of $\alpha = -4$. Note that the Carnoban-Starling equation ($\alpha = -1$) does not yield the best predictions, even though it is the "best" hard sphere equation of state.

Several isotherms were chosen to examine the sensitivity of the results to the value of α , on a finer scale. These results are given in Table 5-3. For the liquid phase isotherms a value of $\alpha = -4.3$ seems to be optimal. The supercritical data are best fit with α of -4.0 or -4.1. It was decided to use a constant value of $\alpha = -4.2$ to fit all of the argon data.

With α set at -4.2 the value of χ and f could then be determined. The optimum values of χ found were correlated as a polynomial in inverse temperature. For this analysis the characteristic parameters were chosen to be equal to the critical parameters. The form that fit χ best was

$$\begin{aligned} \chi = & 0.12342 + \frac{0.15069}{\tilde{T}} - \frac{0.18545}{\tilde{T}^2} + \frac{0.15947}{\tilde{T}^3} \\ & - \frac{0.070261}{\tilde{T}^4} + \frac{0.012111}{\tilde{T}^5} \end{aligned} \quad (5-13)$$

TABLE 5-2
REGRESSION ANALYSIS OF ARGON DATA

\tilde{T}	Average Absolute Deviation in C for $= \alpha$				
	0	-1	-3	-4	-5
0.5966	0.0101	0.0102	0.0094	0.0058	0.7266
0.6297	0.0392	0.0395	0.0361	0.0219	1.3274
0.6629	0.0785	0.0789	0.0714	0.0427	1.7500
0.6960	0.1225	0.1228	0.1100	0.0642	2.0472
0.7292	0.1651	0.1651	0.1461	0.0830	2.2372
0.7623	0.2062	0.2059	0.1798	0.0983	---
0.7954	0.2445	0.2436	0.2094	0.1085	2.3746
0.8286	0.2758	0.2736	0.2304	0.1104	2.3629
0.8949	0.3104	0.3056	0.2408	0.1122	2.1992
0.9280	0.3053	0.2990	0.2374	0.1280	2.0497
0.8617	0.2994	0.2963	0.2430	0.1071	2.2885
1.1	0.2840	0.2764	0.2142	---	1.4495
1.2	0.2413	0.2344	0.1835	0.1260	1.1049
1.3	0.2175	0.2088	0.1580	0.1058	0.8986
1.4	0.1990	0.1899	0.1383	0.0912	---
1.5	0.1837	0.1740	0.1227	0.0801	0.6364
1.6	0.1707	0.1611	0.1101	0.0713	0.5516
1.7	0.1611	0.1504	0.1003	0.0643	0.4845
1.8	0.1530	0.1411	0.0920	---	---
1.9	0.1498	0.1344	0.0854	0.0536	0.3864
2.0	0.1403	0.1286	0.0798	0.0495	0.3505
2.2	0.1310	0.1196	0.0713	0.0425	0.2948
2.4	0.1242	0.1131	0.0651	0.0371	0.2536
2.6	0.1192	0.1084	0.0610	0.0324	0.2214
2.8	0.1152	0.1047	0.0582	0.0290	0.1960
3.0	0.1126	0.1023	0.0566	0.0261	0.1749

TABLE 5-3
EFFECT OF HS EQUATION ON FITTING ARGON DATA

\tilde{T}	Average Absolute Deviation in C for $\alpha = \alpha$						
	-3.8	-3.9	-4.0	-4.1	-4.2	-4.2	-4.4
.7954	.1435	.1277	.1085	.0848	.0547	.0214	.0401
.8286	.1516	.1329	.1104	.0831	.0535	.0263	.0595
.8617	.1507	.1297	.1071	.0829	.0592	.0399	.0866
.8949	.1477	.1294	.1122	.0916	.0732	.0667	.1264
.9280	.1581	.1434	.1280	.1144	.1049	.1152	.1851
1.1	.1484	.1368	.1309	.1235	.1258		
1.2	.1344	.1303	.1260	.1263	.1364		
1.3	.1126	.1092	.1058	.1064	.1065		
1.8	.0607	.0590	.0585	.0618	.0698		

The maximum error in calculated x values from equation 5-13 was 0.105% with an average error 0.022%. With x values from equation 5-13 and α set at -4.2 the optimal values of f were then found. These values were also fit to a polynomial as

$$f = -1.4098 + \frac{14.70}{\tilde{T}} - \frac{23.237}{\tilde{T}^2} + \frac{25.221}{\tilde{T}^3} - \frac{11.636}{\tilde{T}^4} + \frac{2.0463}{\tilde{T}^5} \quad (5-14)$$

This polynomial form reproduced the f values with an average error of 0.15% for the isotherms analyzed. The temperature dependence of x and f is shown in Figure 5-4. Table 5-4 gives a summary of the values of x and f for argon along with the average error in the prediction of the direct correlation function integrals. In general, the correlation function integrals were correlated to within the experimental accuracy. The only range of temperatures for which the fit was not excellent was near the critical point, which is to be expected.

Analysis of Methane Data

There is less high quality P-V-T data available for dense methane than for argon. In this work the equation

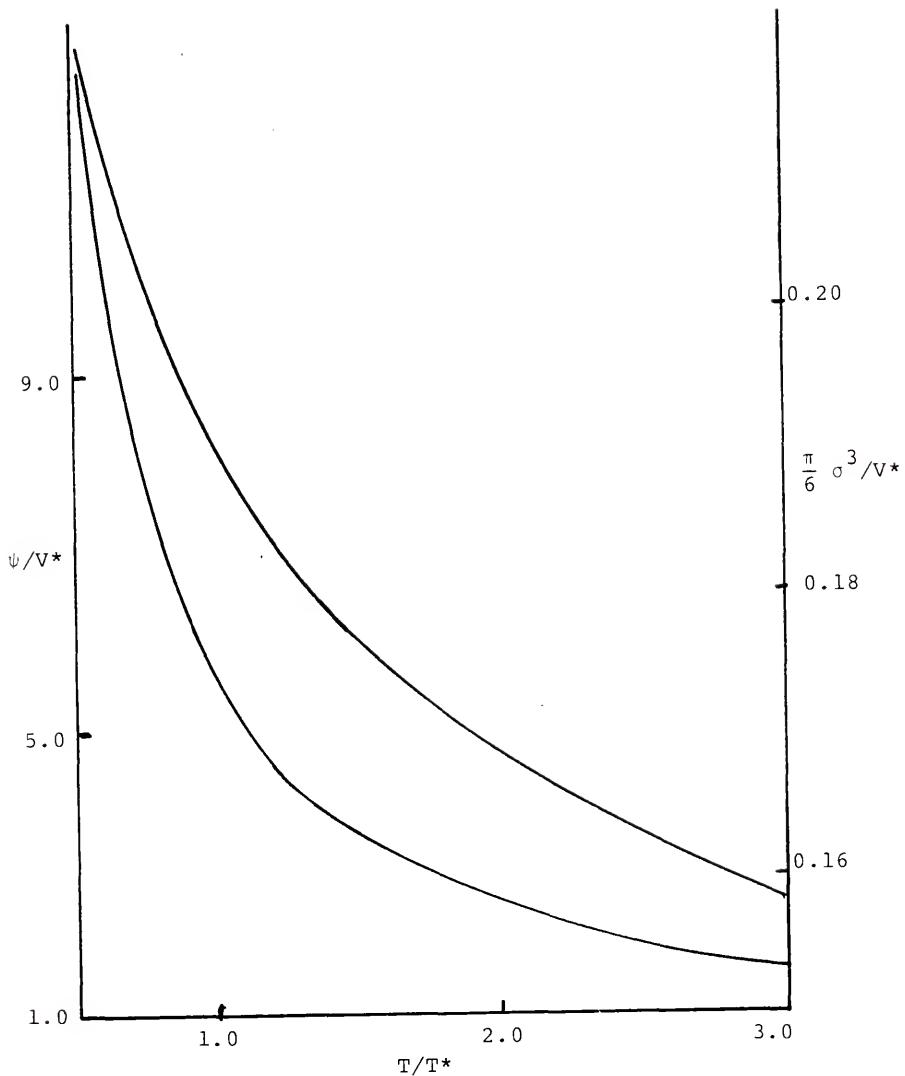


Figure 5-4. Dimensionless hard sphere diameter and perturbation function based on argon reference.

TABLE 5-4
CORRELATION OF ARGON DCFI USING $\alpha = -4.2$

\tilde{T}	X	f V _C	Average Error in \bar{C}
0.5966	0.21159	890.79	.0035
0.6297	0.20916	820.09	.0128
0.6629	0.20692	759.79	.0525
0.6960	0.20482	707.47	.0372
0.7292	0.20283	661.13	.0466
0.7623	0.20094	620.05	.0532
0.7954	0.19915	583.39	.0562
0.8286	0.19745	550.40	.0547
0.8617	0.19583	520.61	.0596
0.8949	0.19430	493.31	.0732
0.9280	0.19286	467.98	.1076
1.1	0.18649	373.74	.1264
1.2	0.18348	335.43	.1377
1.3	0.18086	306.28	.1166
1.4	0.17852	282.27	.1037
1.5	0.17643	262.19	.0936
1.6	0.17453	245.04	.0844
1.7	0.17280	230.17	.0764
1.8	0.17120	217.10	.0700
1.9	0.16971	205.48	.0648
2.0	0.16833	195.05	.0605
2.2	0.16582	177.04	.0527
2.4	0.16359	161.94	.0458
2.6	0.16159	149.05	.0393
2.8	0.15978	137.88	.0343
3.0	0.15814	128.10	.0308

of state of Mollerup (1980) was used to generate nine subcritical isotherms and one supercritical isotherm, as was done for argon. These supercritical isotherms measured by Robertson and Babb (1969) were also analyzed. The procedure used for the analysis of the methane data was the same as for argon, except some positive values of α were also investigated.

For the liquid phase isotherms a value of $\alpha = -4.2$ was clearly the best. For the supercritical data values of α from -3.0 to -4.3 could produce almost equivalent results, but $\alpha = -4.0$ was the optimum. It should be noted that for the supercritical isotherm values of $\alpha = 9$ could also offer a reasonable representation of the data, but not as good as -4.0. Thus, a value of -4.2 was chosen to represent the methane data.

Proceeding as was done before for the argon analysis, the values of X and f were fit to polynomials in inverse temperature. The resultant forms were

$$X = 0.13832 + \frac{0.026446}{\tilde{T}} + \frac{0.080054}{\tilde{T}^2} - \frac{0.089994}{\tilde{T}^3} + \frac{0.039085}{\tilde{T}^4} - \frac{0.0060984}{\tilde{T}^5} \quad (5-15a)$$

$$f = 5.0851 - \frac{23.21}{\tilde{T}} + \frac{50.827}{\tilde{T}^2} - \frac{40.662}{\tilde{T}^3} + \frac{15.818}{\tilde{T}^4} - \frac{2.3173}{\tilde{T}^5} \quad (5-15b)$$

where the critical properties were used as the reducing parameters. These functions are plotted in Figure 5-5. Table 5-5 gives the summary of results for the methane correlation. The proposed model was able to reproduce the data to within the experimental uncertainty.

Use of the Correlations to Calculate Pressure Changes

The development of the DCFI models for the pure components was first tested by performing equation of state calculations for the base substances, argon and methane. The method of calculation was to choose the lowest density point on each isotherm as a reference and then to calculate pressure changes for all other points on the isotherm from that reference. There are thus two criteria for goodness of fit, the average percent error in pressure changes, defined by

$$\overline{\Delta P} = \left\{ \sum_{i=1}^{ND} \left[\frac{\Delta P_i^{\text{calc}} - \Delta P_i^{\text{exp}}}{\Delta P_i^{\text{exp}}} \right] \right\} / ND \quad (5-16)$$

and the sum squared percent error, defined by

$$SSE\Delta P = \left\{ \sum_{i=1}^{ND} \left[\frac{\Delta P_i^{\text{calc}} - \Delta P_i^{\text{exp}}}{\Delta P_i^{\text{exp}}} \right]^2 \right\} \quad (5-17)$$

where in both cases ND is the total number of data points for a compound. When parameters were found to best "fit" a set of data, the quantity SSE ΔP was minimized using a

TABLE 5-5
CORRELATION OF METHANE DCFI USING $\alpha = -4.2$

\tilde{T}	X	$f V_c$	Average Error in \bar{C}
.4986	.22182	1545.26	.0015
.5511	.21596	1309.43	.0155
.6036	.21095	1131.07	.0188
.6561	.20671	996.35	.0157
.7085	.20302	890.93	.0140
.7610	.19974	805.32	.0335
.8135	.19675	733.53	.0612
.8660	.19400	671.78	.0946
.9185	.19145	617.18	.1413
1.1	.18381	473.60	.1484
1.6173	.16916	260.80	.2262
1.9585	.16316	204.86	.1437
2.4833	.15703	168.74	.0637

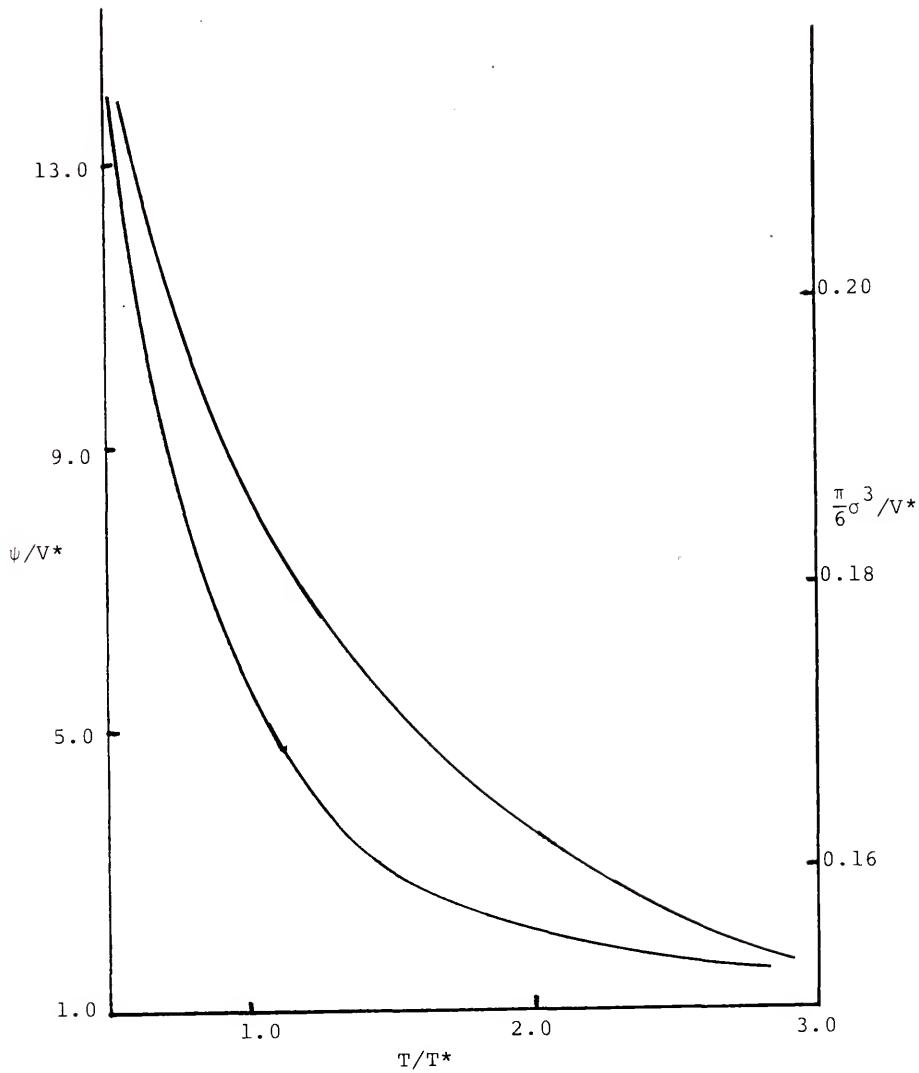


Figure 5.5. Dimensionless hard sphere diameter and perturbation functions based on methane reference.

nonlinear regression routine and the program GROUPFIT listed in Appendix 6. However, the data comparisons will normally be made in terms of the quantity $\overline{\Delta P}$. This procedure is common and is used to eliminate bias from the error minimization.

The first test performed was to calculate $\overline{\Delta P}$ for argon using the characteristic parameters as the critical parameters and the functions given by equations 5-13 and 5-14. The average error was found to be 1.42%. This is larger than expected, but if only the liquid phase data are reconsidered, the error is just 0.629%, and if the isotherm that is within 10% of the critical temperature is neglected, the error for the liquid isotherms is only 0.34%. This is within the accuracy of the equation of state for this region of the phase diagram. On the whole the largest errors are found in the low density data near the critical temperature. The equation is able to reproduce the highest temperature isotherms ($T/T_c = 2.8$ and 3.0) with an average error of 0.47%. So the fit of the argon data seems satisfactory for the desired usage.

In an attempt to improve the argon representation, a regression was performed to find the set of characteristic parameters that minimized the sum square error in the pressure changes as per equation 5-17. The parameters found were $T^* = 144.45$ K and $V^* = 74.31 \text{ cm}^3/\text{gmole}$ as compared to $T_c = 150.86$ K and $V_c = 74.57 \text{ cm}^3/\text{gmole}$. The average

error for all of the data increased to 1.53%. This worsening of the percentage error occurred because the fit was made more even; that is, $SSE\Delta P$ was decreased from 4.549×10^5 to 3.034×10^3 , but on the average the error was larger. This is due to the larger localization of error in the critical region.

A calculation was also performed on the methane data using the argon functions and methane's critical parameters as the characteristic parameters; the error was 3.13%. And when a regression was performed on the methane data, the characteristic parameters were found to be $T^* = 190.54$ K and $V^* = 98.40 \text{ cm}^3/\text{gmole}$ (compare $T_c = 190.53$ K and $V_c = 98.52 \text{ cm}^3/\text{gmole}$) with an error of 2.98%. This shows that the trends found for the methane DCFI as compared to argon carries over to the pressure change calculations.

Similar calculations to those described above were performed using the hard sphere diameter and perturbation term functions as given by equations 5-15. The average error in pressure changes for all of the methane data was 0.57% with the largest error from the isotherm at 175 K (within 9% of the critical temperature). Even at this temperature the high density data are well described. In the reduced temperature range of 0.5 to 0.89 the average error was only 0.18%, well within the accuracy of the data. As for argon, when the GROUPFIT program was employed to find optimal characteristic parameters for methane, the

SSE ΔP was reduced from 4.13×10^2 to 2.44×10^2 , but the average error was increased to 0.727%. Again the localization of the error causes this phenomenon.

A calculation of the pressure changes for the argon data using the methane functions gave an error of 4.65%, and when optimized, the argon characteristic temperature only changed 1.3% and the error reduction was only to 4.56%. This again shows that there are noticeable differences in the compressive behavior of argon and methane at high densities.

In summary, the temperature dependence of the hard sphere diameter and perturbation term in the DCFI model are seen to adequately represent the data from which they were developed. The difference in DCFI noticed for the atomic species argon and the polyatomic methane are noticeable in calculations of compressions.

The rest of this work will deal with calculations of hydrocarbon compressions using the group contribution formulation. The groups of interest are methyl ($-\text{CH}_3$) and methylene ($-\text{CH}_2$). These are physically more similar to methane than to argon. For this reason all of the group contribution calculations will be performed using the methane reference functions.

CHAPTER 6
USE OF THE GROUP CONTRIBUTION MODEL FOR
PURE FLUIDS

The development thus far has been limited to the formal expressions for calculating property changes of mixtures based on the group contribution model of direct correlation function integrals and the parameterization of the model using data for argon and methane. In both cases the molecules were assumed to consist of only one type of group. This chapter presents the calculations of pressure changes for pure fluids composed of different types of groups.

The first section discusses the extension of the correlations required for systems of several groups. The remainder of the chapter presents and discusses the results of the calculations performed for several n-alkanes and one n-alkanol.

Extension of the Model to Multigroup Systems

The expressions developed in Chapter 4 for calculation of pressure changes involve two contributions.

$$\Delta P\beta = \Delta P\beta^{\text{HS}} + \Delta P\beta^{\text{PERTURBATION}} \quad (6-1)$$

The hard sphere contribution is calculated for the solution of groups using the results shown in Appendix 5. To calculate the perturbation contributions for multigroup systems, the form of the $\psi_{\alpha\beta}$ functions must be established for the terms with $\alpha \neq \beta$. In Chapter 5 a corresponding states expression was developed

$$\psi_{\alpha\alpha} = v_{\alpha\alpha}^* f(T/T_{\alpha\alpha}^*) \quad (6-2)$$

where f is a universal function of the reduced temperature. This result is extended to the unlike terms as

$$\psi_{\alpha\beta} = v_{\alpha\beta}^* f(T/T_{\alpha\beta}^*) \quad (6-3)$$

and the characteristic parameters are found from

$$v_{\alpha\beta}^* = \frac{1}{8} [(v_{\alpha\alpha}^*)^{1/3} + (v_{\beta\beta}^*)^{1/3}] \quad (6-4a)$$

$$T_{\alpha\beta}^* = (T_{\alpha\alpha}^* T_{\beta\beta}^*)^{1/2} (1 - k_{\alpha\beta}) \quad (6-4b)$$

where $k_{\alpha\beta}$ is an empirically determined binary interaction parameter for groups α and β . It is important to note that this binary parameter can still be determined from analysis of pure component volumetric data.

Designation of Groups

Before the group contribution model can be used for calculation of property changes, the decision as to which collections of atoms in a molecule comprise a group must be made. The simplest choice would be to consider each atom as a group, and thus the properties of all molecules could be described with minimal information. However, that is an overly ambitious approach. Even for the molecules considered here that contain only carbon, hydrogen, and oxygen atoms, this is unworkable. Typically, the common organic radicals are designated as the groups.

For this work it must be decided if the n-alkanes are composed of only one type of group, or two. If they are considered as being comprised of only one type of group, then the model could never predict excess volumes for n-alkane mixtures. This is reasonable at low pressures, but for highly compressed systems, noticeable excess volumes do exist (Snyder, Benson, Huang, and Winnick, 1974). Thus, the n-alkanes will be considered to be composed of two groups, methyl (CH_3) and methylene (CH_2). To analyze methanol the hydroxyl moiety (OH) will also be considered as a separate group.

Pressure Change Calculations

All of the molecules analyzed in this work will be considered to be composed of only two types of groups.

The equations required for the calculation of the pressure changes are

$$P\beta - (P\beta)^{\text{ref}} = P\beta^{\text{HS}} - (P\beta^{\text{HS}})^{\text{ref}}$$

$$- \frac{1}{2} (\rho^2 - (\rho^2)^{\text{ref}}) (v_1^2 \psi_{11} + 2v_1 v_2 \psi_{12} + v_2^2 \psi_{22}) \quad (6-5)$$

where here, v_i is the number of groups of type i in the molecule. The individual terms are found using

$$\begin{aligned} P\beta^{\text{HS}} = & \frac{1}{\pi} \left\{ \frac{\xi_0}{1-\xi_0} + \frac{3\xi_1 \xi_1}{(1-\xi_3)^2} + \frac{3\xi_2^3}{(1-\xi_3)^3} \right. \\ & \left. - 4 \cdot 2 \frac{\xi_3 \xi_2^3}{(1-\xi_3)^3} \right\} \end{aligned} \quad (6-6a)$$

with

$$\xi_\ell = \frac{\pi}{6} \rho [v_1 \sigma_1^\ell + v_2 \sigma_2^\ell] \quad (6-6b)$$

and the σ_i terms are found using

$$\frac{\pi}{6} \sigma_i^3 / v_i^* = f(T/T_i^*) \quad (6-6c)$$

where the function of reduced temperature required in equation 6-6c is given in Chapter 5. The perturbation contributions are found using equations 6-3 and 6-4 with the required function of reduced temperature again given in Chapter 5.

These functional forms are dependent only on the reference component chosen for their development, either argon or methane. For the two group molecules there are then only five independent parameters, V_1^* , V_2^* , T_1^* , T_2^* , and k_{12} .

Analysis of n-Alkane Compressions

In this section we consider the ability of the proposed formulation to calculate changes in pressure during compression of four n-alkane molecules: ethane, propane, n-pentadecane, and n-octadecane. Calculation of pressure changes using the equations given above were performed for both the argon- and methane-based reference functions as derived in Chapter 5.

The initial plan of attack was to determine the methyl parameters using ethane data and ethylene and cross parameters from the propane data. The model capabilities would then be examined by using these same parameters for calculations on the long chain molecules. The analysis was performed both with and without a binary interaction coefficient. The characteristic parameters for the methyl and methylene groups as determined by regression analysis are shown in Table 6-1 along with the errors in calculated pressure changes. Several conclusions can be drawn from these results that will be of future interest. First, the best fit of all of the data was obtained using the methane-based correlations with the inclusion of a binary

TABLE 6-1
CHARACTERISTIC PARAMETERS AND ERROR IN PRESSURE CHANGES FROM ANALYSIS
OF COMPRESSION DATA FOR ETHANE AND PROpane

Parameter Set	Characteristic Temperatures (K)	Characteristic Volumes (cm ³ /gmole)	Interaction Constants	Average Absolute % Error in Pressure Change
1 ^a	CH ₃	CH ₂	CH ₂	k
1 ^a	284.5	422.9	66.77	40.91
2 ^a	284.5	434.0	66.77	48.71
3 ^b	280.7	474.0	66.82	42.94
4 ^b	280.7	397.0	66.82	47.17
Ethane	Propane	Ethane	Propane	Ethane
5 ^c	307.0	361.6	145.5	200.3

				1.57
				2.80

^ausing argon-based correlations

^busing methane-based correlations

^cusing methane-based correlations treating ethane and propane as molecules not groups

interaction coefficient. This binary constant was much larger than usual and thus gave a large value of the T_{12}^* parameter. This results from the fact that the model is much more sensitive to the values of the characteristic volumes than the characteristic temperatures so that large adjustments to the binary constant are required to significantly affect the calculations.

It was also seen that $2V_{\text{CH}_3}^* = 0.9 V_{\text{C,ethane}}$ and $2V_{\text{CH}_3}^* + V_{\text{CH}_2}^* = 0.9 V_{\text{c,propane}}$. This suggests an approach for estimating characteristic volumes of the groups from critical properties. The characteristic temperatures might also be obtainable using critical values with some sort of mixing rule applied.

While the results are not as good as the molecular fit, they could be satisfactory. A more important question is their ability to predict compression data for other hydrocarbons. For n-pentadecane and n-octadecane results were rather poor, the best agreement being an average error in the pressure changes of 16.6% using parameter set 1. This is discouraging but not unexpected. The hard sphere contribution does not behave properly at high densities as explained in Appendix 5. In addition, the improper ideal gas limit of the equation of state affects the results.

In an effort to improve the model performance, the data for the two long chain hydrocarbons were used to determine the methylene and interaction parameters.

The results of interest are shown in Table 6-2. The methyl parameters were those found from analysis of the ethane data. The results are rather encouraging in that either the four- or five-parameter models could give an adequate representation of data for both short- and long-chain hydrocarbons. However, it should be noted that none of the parameter sets could give a reasonable representation of the propane pressure changes.

These results do yield two interesting conclusions. First, that when the larger hydrocarbons are considered for the parameter estimation that the binary parameter becomes very important. Noticeable improvement in the pressure change calculations occurs when the binary parameter is included. This suggests that the methyl and methylene groups should be considered as distinct entities. However, the magnitude of the binary parameter is much greater than would be expected. It can also be seen that the methane-based correlations are more apropos for modeling the alkane compounds because the groups are physically more akin to methane than to argon.

After studying the aforementioned results, it was decided to establish a final set of model parameters for the methyl and methylene groups from an analysis of all of the n-alkane data simultaneously. The methane-based reference functions were used, and the calculations were performed both with and without a binary parameter. These

TABLE 6-2

CHARACTERISTIC PARAMETERS FOR THE METHYLENE GROUP AND BINARY INTERACTION
CONSTANT DETERMINED BY REGRESSION OF DATA FOR N-PENTADECANE
AND N-OCTADECANE

Parameter Set	Characteristic Temperature $T_{\text{CH}_2}^*$ ($^{\circ}\text{K}$)	Characteristic Volume $V_{\text{CH}_2}^*$ (cm^3/gmole)	Interaction Constant $\kappa_{\text{CH}_2-\text{CH}_3}$	C ₁₅	C ₁₈	Total
6 ^a	564.5	40.41	0.2678	2.5	4.0	3.2
7 ^a	534.0	40.85	0.0	2.7	4.4	3.5
8 ^b	572.3	40.75	0.1846	1.9	3.2	2.5
9 ^b	552.6	41.20	0.0	2.2	3.5	2.8

^a argon reference functions

^b methane reference functions

results are shown in Table 6-3. It can be seen that use of a binary parameter does improve the results and that the order of magnitude of this parameter is reasonable. Using only five adjustable parameters, the average absolute error in pressure changes calculated for all four hydrocarbons was 5.9%.

Analysis of Methanol Compressions

A set of compression measurements for methanol were analyzed to determine if the present model could adequately calculate pressure changes for molecules other than n-alkanes. Methanol was considered to be composed of one methyl group and one hydroxyl (OH) group. The methyl group characteristic parameters used are those listed under parameter set 11 in Table 6-3. The regression results are shown in Table 6-4. The characteristic volume for the hydroxyl group appears to be quite reasonable because $V_{CH_3}^* + V_{OH}^* \approx 0.9 V_{c,methanol}$ which is the same pattern seen for the alkanes. The characteristic temperature and binary parameter found are surprising, but these values were necessary to obtain a fit of the data about as good as that for the alkanes.

Summary

While the calculations presented here are based on recognized assumptions that are believed to be sound, there

TABLE 6-3

CHARACTERISTIC PARAMETERS FOR METHYL AND METHYLENE GROUPS DETERMINED FROM ANALYSIS OF ALL N-ALKANE DATA USING THE METHANE-BASED CORRELATIONS

Parameter	Characteristic Set	Characteristic Temperature (K)	Characteristic Volume (cm^3/gmole)	Interaction Constant	Average Error in Pressure Change (%)	Total	C_2	C_3	C_{15}	C_{18}
	CH ₃	CH ₂	CH ₃	CH ₂						
10	293.3	449.0	67.64	40.27	0.0	6.1	4.9	9.5	5.3	4.9
11	293.4	461.6	67.61	40.29	0.0198	5.9	4.7	9.4	5.0	4.6

TABLE 6-4
HYDROXYL GROUP CHARACTERISTIC PARAMETERS AND METHYL-HYDROXYL INTERACTION
PARAMETER DETERMINED FROM ANALYSIS OF METHANOL COMPRESSIONS

Parameter Set	Hydroxyl Characteristic Temperature (K)	Hydroxyl Characteristic Volume (cm ³ /gmole)	Hydroxyl-Methyl Interaction Constant	Average Error in Pressure Changes for Methanol (%)
12	774.1	29.97	0.0	7.2
13	632.7	31.31	-0.1978	6.6

are certain disconcerting aspects. In particular, the equation of state developed does not properly approach the ideal gas limit. Even though the calculations are always performed for pressure differences from a liquid, or dense fluid, reference state this may be important.

Also, the percentage errors in the pressure change calculations appear to be rather large. In most process design calculations the temperature and pressure are known and one wishes to calculate the volume. It would then be of interest to know how the present model would perform in calculating volume changes for given pressure changes. A simple error analysis shows how this can be estimated. At constant temperature errors in pressure calculations and volume calculations are related by

$$\Delta V = \left(\frac{\partial V}{\partial P} \right)_T \Delta P \quad (6-7)$$

Then average absolute errors in volumes and pressures must be related by

$$\left| \frac{\Delta V}{V} \right| / = P \beta_T \left| \frac{\Delta P}{P} \right| / \quad (6-8)$$

where β_T is the isothermal compressibility. For liquids the product $P \beta_T$ is almost always less than 0.2 and even then is only that large at very high pressures. This suggests that if the present correlation were used to calculate

a volume change for a given pressure change that the average absolute errors would be less than 20% of the errors reported here for the pressure changes. This shows that the present model compares reasonably with existing correlations.

One reassuring result of regression analysis is the magnitude of the group characteristic volumes that were calculated. Ratios of the group characteristic volumes found here are very nearly equal to the ratios of the van der Waals volumes for these groups. This may allow for estimation of these group parameters. This type of regularity was not seen for the group characteristic temperatures. Also, whereas the characteristic volumes for the different groups did not vary much when determined from different data sets, the characteristic temperatures did. As a result, the binary constants did not follow a pattern. The binary constant was necessary in all cases to obtain an optimal representation of the data, but the improvement obtained by introducing this additional parameter was minimal.

No calculations have been reported for chemical potential changes or for pressure changes for multicomponent systems. The necessary formulae have been presented in Chapter 4 and Appendix 5. Pressure change calculations for multicomponent systems are no more difficult than those reported here because the molecules considered contained more than one group.

CHAPTER 7 DISCUSSION

This work has centered on the development of a group contribution liquid phase equation of state. Fluctuation solution theory was used to develop the exact relationships between thermodynamic derivatives and direct correlation function integrals. Two approximations were made to actually construct the equation of state. The first approximation made was the use of the interaction site formalism, or RISM theory. The last stage in the model formulation was the choice of an approximate form for the group direct correlation function integrals. After that development, the general expressions for calculation of pressure and chemical potential changes were written and used for several compounds.

In this chapter, the important aspects of each stage in the development described above will be examined in detail. Great emphasis will be placed on the approximations embodied in the model development as they pertain to the numerical results.

Fluctuation Solution Theory

The relationship between integrals of molecular correlation functions and thermodynamic derivatives have come to be known as fluctuation solution theory (O'Connell, 1981). Kirkwood and Buff (1951) originally reported these relationships though they have not been extensively used. The original results, using total correlation function integrals, are valid for both spherical and molecular systems. With the introduction of the direct correlation functions, through the Ornstein-Zernike equation, the analysis is not as simple. Appendix 1 details a procedure which surmounts all difficulties encountered. This result is not new, but the rigorous proof appears to be. This result could also be derived through the use of the operator technique of Adelman and Deutch (1975).

Approximations

While equations 2-24 and 2-25 are exact results for fluctuation derivatives, one must have values for the direct correlation function integrals for these to be useful. Because exact values of the required integrals are not generally available, some approximations must be used to obtain these values. The approximations used will determine, to a large degree, the success of any thermodynamic calculations. In this work, two levels of approximation are used and they will be discussed separately below.

Group Contributions

One of the major goals of this research was the development of a group contribution formulation of fluctuation solution theory. This appears to be a realistic and rational goal. This is true because fluctuation solution theory requires knowledge of correlation functions and correlations among the groups are well defined. The major problem encountered was the ability to separate the inter- and intramolecular correlations. The RISM theory (Chandler and Andersen, 1972) purports to affect this separation and offer an approximate relationship between group direct correlation functions and molecular correlations. The calculations reported here are based on this original version of the RISM theory.

Recently, the direct correlation functions calculated using the RISM theory have become the objects of considerable attention (Cummings and Stell, 1981, 1982b; Sullivan and Gray, 1981). It has been shown that in many situations for neutral molecules that the site-site direct correlation functions are necessarily long-ranged. This means that these functions are nonintegrable and thus no compressibility relation involving these functions may exist. Cummings and Stell (1982a) have shown how a general compressibility relation can be derived in terms of a limiting operation, but this is not a practical solution. However, for the cases that have been considered in the literature it seem

this problem can be overcome. If the compressibility relation is viewed as the $k \rightarrow 0$ limit of a result in Fourier space, where all of the correlation function transforms exist, then all of the mathematical manipulations required may be performed. Then as the long wavelength limit is taken, we find (Appendix 7) the following relationship:

$$\left(\frac{\partial p_\beta}{\partial p} \right)_{T, \underline{x}} = 1 - \rho \sum_{ij} \sum_i x_i x_j \sum_{ab} v_{ia} v_{jb} \hat{C}_{\alpha\beta}(0) \quad (7-1)$$

While the individual functions $C_{\alpha\beta}(r)$ may be long-ranged, it appears that the collection of terms $\underline{w} \underline{C} \underline{w}$ is well defined in the $k \rightarrow 0$ limit. It is known (Cummings and Stell, 1982a) that for diatomic molecules this is true, and thus a simple compressibility theorem applies. Also for triatomics, as examined by Cummings and Stell (1981), we find that this summation of terms is nondivergent. As has now become known, the possible divergencies in the $C_{\alpha\beta}(r)$ functions are due to intramolecular effects that are not shown explicitly. It appears that the projection by the v matrix removes the divergent terms. This is analogous to the ionic solution case (Perry and O'Connell, 1984) where the charge neutrality constraint removes the divergent part of the direct correlations.

Chandler et al. (1982) formulated the proper integral equation theory for site-site correlations to offer an exact formulation involving nondivergent $C_{\alpha\beta}(r)$ functions

that here are labeled $C_{\alpha\beta}^O(r)$. These new functions are related to the RISM $C_{\alpha\beta}(r)$ functions and are made nondivergent by removal of intramolecular correlations involving only sites α or β . This requires use of auxiliary functions $\Omega_{\alpha\beta}(r)$ that have a complicated density dependence. These functions do possess the interesting property

$$\hat{\Omega}_{\alpha\beta}(0) = \Omega \quad \forall \alpha, \beta \quad (7-2)$$

It is then possible to derive a compressibility relation involving only $C_{\alpha\beta}^O(r)$ function integrals and Ω

$$\left(\frac{\partial P\beta}{\partial \rho}\right)_{T, \underline{X}} = \frac{1}{\Omega} - \rho \sum_{ij} \sum_{\alpha} X_i X_j \sum_{\alpha\beta} v_{i\alpha} v_{j\beta} \int d\vec{r} C_{\alpha\beta}^O(r) \quad (7-3)$$

In this case, the integrals always exist. However, we have no knowledge of the functional dependence of Ω on temperature or density.

One further aspect of the group contribution approach used here needs to be mentioned. This formulation works on the Ansatz that

$$c_{ij}^{(1,2)} = \sum_{\alpha\beta} v_{i\alpha} v_{j\beta} C_{\alpha\beta}(\vec{r}_{\alpha\beta}) \quad (7-4)$$

which is only to be considered an approximate relation. However, the compressibility relation obtained from the above starting point and that found using the proper integral equation formalism (as shown in Appendix 7) are the same. The only difference is that all forms of the RISM theory assume that each group, as opposed to each type of group, have separate correlation, i.e., that the set of functions $c_{ij}^{\alpha\beta}(\vec{r})$ should be considered, not just $c_{\alpha\beta}(\vec{r})$. This is definitely true at the level of the correlation functions themselves. However, it is always possible to define a set of $c_{\alpha\beta}(\vec{r})$ functions that are averages of the $c_{ij}^{\alpha\beta}(\vec{r})$ functions (Adelman and Deutch, 1975) and retain the same compressibility relations.

Modeling of Direct Correlation Function Integrals (DCFI)

As the DCFI are functions of temperature and density, it would be possible to model them using polynomial expansions for the pure fluids and a solution theory for the mixture quantities. In this work, we attempted to use fluctuational forms that have a theoretical basis. This approach seems to have both merits and demerits. For molecules, Mathias (1979) had success in modeling DCFI using an approach suggested by perturbation theory. In the present case this is not of the greatest value because analytic forms are available for group DCFI in only some limited cases (Morris and Perram, 1980; Cummings and Stell, 1982a),

and even then, the solutions are not in closed form. Thus, some reasonable assumptions must be made to proceed with the modeling.

It is known that the RISM correlation functions can be related to Percus-Yevick correlation functions for molecular species in some limiting cases (Chandler, 1976). This led to the use of the form for the DCFI presented in Chapter 5. The important aspect of this approach is that the groups are dealt with as if they were all independent. This is not physically the situation. The dependence is caused by the intramolecular correlations, and they must be properly accounted for to yield an accurate model. Originally it was believed that the RISM theory took account of this behavior, but as was mentioned in the preceding section, this is not true. Even the proper integral equation direct correlation functions, equation 7-3, while short ranged, still involve intramolecular correlations due to third body effects. Cummings and Sullivan (1982a) explicitly show that while the $h_{\alpha\beta}(\vec{r})$ functions are purely intermolecular quantities that the $c_{\alpha\beta}^o(\vec{r})$ are not.

The exact resummation of the cluster expansion for $h_{\alpha\beta}(\vec{r})$ shown by Chandler et al. (1982) suggests a way around the aforementioned difficulties. It should be possible to define a set of direct correlation functions, labeled here as $c_{\alpha\beta}^\psi(\vec{r})$, that include only intermolecular effects. Chandler's (1976) analysis can be examined to see that

these diagrams can be isolated. And then, in the same fashion as was used to eliminate the long-ranged behavior of the original RISM direct correlation functions, it would be possible to write an exact proper integral equation of the form

$$\underline{\underline{\omega}} + \rho \hat{\underline{\underline{h}}} = [\underline{\underline{I}} - \rho \hat{\underline{\underline{W}}}^{\psi}]^{-1} \hat{\underline{\underline{W}}} \quad (7-5)$$

where the elements of the $\hat{\underline{\underline{W}}}$ matrix would contain all information about intramolecular effects. It is then easy to show the relationship between the different classes of direct correlation functions, for example

$$\hat{\underline{\underline{c}}}^{\psi} = \hat{\underline{\underline{c}}} + \frac{1}{\rho} (\hat{\underline{\underline{W}}}^{-1} - \hat{\underline{\underline{\omega}}}^{-1}) \quad (7-6)$$

The elements of the $\hat{\underline{\underline{W}}}$ matrix would be functions of temperature and density, but the exact functionality could not be determined in general. It is possible to identify some of the properties of the new functions, such as

$$\lim_{\rho \rightarrow 0} \hat{\underline{\underline{W}}} = \hat{\underline{\underline{\omega}}} \quad (7-7)$$

and

$$\lim_{k \rightarrow 0} \hat{\omega}_{\alpha\beta} = \hat{W}_{\alpha\beta} \psi_{\alpha,\beta} \quad (7-8)$$

Using equations 7-5 and 7-8, in conjunction with the techniques of Appendix 7, a compressibility relation can be derived in terms of these new group direct correlation functions

$$\left(\frac{\partial P\beta}{\partial \rho}\right)_{T,\underline{X}} = \frac{1}{W} - \rho \sum_{ij} \sum_i X_i X_j \sum_{\alpha\beta} \sum_{i\alpha} v_{i\alpha} v_{j\beta} \int d\vec{r} C_{\alpha\beta}^{\Psi}(\vec{r}) \quad (7-9)$$

All of the above analyses show that there is no simple solution to the modeling problem. One may either work with a simple compressibility relation written in terms of DCFI whose behavior is not certain, or in terms of well behaved DCFI but have another unknown quantity present. The former approach was taken for this work and is discussed below.

DCFI Model

The rationale behind the development of the DCFI model has been presented in Chapter 5. It is of interest to note that the proposed form is a group variation of a van der Waals, or mean field, model. Appendix 2 details how higher order correction terms could be appended to the proposed form.

Because the DCFI model was formulated as a corresponding states correlation, the constants in the temperature

dependence of the hard sphere diameters and perturbation terms had to be determined using experimental data. Volumetric data for both argon and methane were used to accomplish this task. The results of the compression calculations show that the methane-based correlations were definitely superior for representation of the properties of the larger molecules.

Comparison Calculation

Chapter 6 presents the results of the group contribution compression calculations for the n-alkane and methanol. The results seem to indicate that the theoretical basis is feasible but that the accuracy is not that desired. It is an accomplishment to be able to perform the compression calculations for all of the n-alkanes using only five parameters, but the overall accuracy is not high. One would hope to be able to calculate pressure changes with an accuracy of about 1% (this allows for density change calculations accurate to ~0.2%), and this cannot be assured.

The theoretical basis behind the equation of state development is now on firm footing. Our compressibility relation is exact; one must simply have proper models for the functions involved. Here, this appears to not be the case. Because we use the RISM approximation, the $c_{\alpha\beta}(r)$ functions must contain intramolecular effects that have no analogy at the molecular level. Thus, our model that

is based on an analogy to a previously successful molecular approach appears inadequate. Note, however, that we seem to have little recourse. Because if we were to introduce easily modelable $c_{\alpha\beta}(r)$'s, then the aspect of determining the W function must be addressed, and this is still an unsolved problem.

Summary

This study has revealed many interesting aspects about site-site correlation functions and their relationship to thermodynamic derivatives. A group contribution liquid reference state equation of state has been formulated and tested. The results are encouraging enough to warrant further investigation but not accurate enough for practical density calculations. It appears that the major problem associated with the present approach is the inability to model the required functions, and suggestions have been made as to how one can alleviate that problem.

CHAPTER 8 CONCLUSIONS

The goal of this work was the development of a group contribution technique for calculation of liquid phase properties of mixtures. The general results are available but have only been tested on a few pure components. The calculated pressure changes for four n-alkanes and methanol are in general in error by less than 7%. This is reasonable but not of high enough accuracy for process engineering calculations. While the results of this study are not outstanding, there are several interesting conclusions that can be drawn.

It has been shown that it is possible to derive thermodynamic property derivatives from a RISM theory. A generalized compressibility theorem was proven, and this was used along with a model, based on a rigorous perturbation theory, to develop a van der Waals equation of state.

The liquid phase equation of state was applied to the representation of compression measurements of argon and methane. It was shown that proper choice of the repulsive contribution to the equation of state is important. Also, that an optimum repulsive contribution

could be determined from a new hard sphere equation of state.

The use of the group contribution model was limited. Pressure changes could be calculated for both long- and short-chain alkanes using a five-parameter model. The results were of reasonable accuracy for these cases and when the model was applied to methanol. While the volumetric parameters in the model appeared to correlate well with previous molecular results (Mathias, 1979), the temperature parameters followed no pattern.

An analysis of the present work also shows several areas that require future work. First, the present model should be applied for calculation of chemical potential changes for n-alkane mixtures. This, along with mixture volumetric calculations, would be a strong test of the model's ability. Secondly, some effort to identify the intramolecular correlation functions of the form shown in Chapter 7 may be required to improve the present model. This appears to be the weakest aspect of the present work.

APPENDIX 1
 FLUCTUATION DERIVATIVES IN TERMS OF DIRECT CORRELATION
 FUNCTION INTEGRALS

To eliminate the difficulties associated with the form of the general O-Z equation we define an angle averaged total correlation function, $\langle h_{ij}(R_1, R_2) \rangle$ by

$$\langle h_{ij}(R_1, R_2) \rangle = \frac{1}{\Omega^2} \int d\Omega_1 d\Omega_2 h_{ij}(1, 2) \quad (\text{Al-1})$$

and then we implicitly define a new set of direct correlation functions, the $\langle c_{ij}(R_1, R_2) \rangle$ by an O-Z type equation

$$\begin{aligned} \langle h_{ij}(R_1, R_2) \rangle &= \langle c_{ij}(R_1, R_2) \rangle \\ &+ \sum_k \frac{\langle N_k \rangle}{V} \int dR_3 \langle c_{ik}(R_1, R_3) \rangle \langle h_{kj}(R_3, R_2) \rangle \quad (\text{Al-2}) \end{aligned}$$

Now, because the full $h_{ij}(1, 2)$ is translationally invariant, the average function must also be, and thus the $\langle c_{ij} \rangle$ function must also possess this property. Then if we integrate equation Al-2 over one coordinate we have

$$\begin{aligned} \langle h_{ij}(R) \rangle &= \langle c_{ij}(R) \rangle \\ &+ \sum_k \frac{\langle N_k \rangle}{V} \int ds \langle c_{ik}(s) \rangle \langle h_{kj}(R-s) \rangle \quad (\text{Al-3}) \end{aligned}$$

And if this is then integrated once more we find

$$\langle h_{ij} \rangle = \langle c_{ij} \rangle + \sum_k \langle N_k \rangle \langle c_{ik} \rangle \langle h_{kj} \rangle \quad (\text{A1-4})$$

where we define

$$\langle h_{ij} \rangle = \frac{1}{V} \int dR \langle h_{ij}(R) \rangle \quad (\text{A1-5a})$$

$$\langle c_{ij} \rangle = \frac{1}{V} \int dR \langle c_{ij}(R) \rangle \quad (\text{A1-5b})$$

and when these terms are collected in matrix form we find

$$\langle \underline{\underline{h}} \rangle = \langle \underline{\underline{c}} \rangle + \langle \underline{\underline{c}} \rangle \langle \underline{\underline{N}} \rangle \langle \underline{\underline{h}} \rangle \quad (\text{A1-6})$$

Here, the terminology is the same as that used in Chapter 2 for the definition of the matrix elements. This relation becomes most useful when it is realized that

$$\langle \underline{\underline{h}} \rangle = \underline{\underline{H}} \quad (\text{A1-7})$$

as can be shown by direct substitution. And now rearrangement leads to

$$[\underline{\underline{N}} + \underline{\underline{N}} \underline{\underline{H}} \underline{\underline{N}}]^{-1} = [\underline{\underline{N}}^{-1} - \langle \underline{\underline{c}} \rangle] \quad (\text{A1-8})$$

which shows that the fluctuation derivatives can be written in terms of the integrals of the $\langle c_{ij} \rangle$ functions. The

relation between c_{ij} and $\langle c_{ij} \rangle$ is not obvious but can be derived. By definition

$$\begin{aligned}\langle c_{ij}(\vec{R}_1, \vec{R}_2) \rangle &= \langle h_{ij}(\vec{R}_1, \vec{R}_2) \rangle \\ - \sum_k \frac{\langle N_k \rangle}{V} \int d\vec{R}_3 \langle c_{ik}(\vec{R}_1, \vec{R}_3) \rangle \langle h_{kj}(\vec{R}_3, \vec{R}_2) \rangle\end{aligned}$$

and, if the O-Z equation is angle averaged, we find

$$\begin{aligned}\langle h_{ij}(\vec{R}_1, \vec{R}_2) \rangle &= \frac{1}{\Omega^2} \int d\vec{\Omega}_1 d\vec{\Omega}_2 c_{ij}(1, 2) \\ + \sum_k \frac{\langle N_k \rangle}{V\Omega^3} \int d\vec{\Omega} d\vec{\Omega}_1 d\vec{\Omega}_2 c_{ik}(1, 3) h_{kj}(3, 2)\end{aligned}\quad (\text{A1-9})$$

Now, when these two relations are combined, the link between the angle averaged c_{ij} and the $\langle c_{ij} \rangle$ functions are given as

$$\begin{aligned}\langle c_{ij}(\vec{R}_1, \vec{R}_2) \rangle &= \frac{1}{\Omega^2} \int d\vec{\Omega}_1 d\vec{\Omega}_2 c_{ij}(1, 2) \\ + \sum_k \frac{\langle N_k \rangle}{V\Omega^3} \int d\vec{\Omega} d\vec{\Omega}_1 d\vec{\Omega}_2 c_{ik}(1, 3) h_{kj}(3, 2) \\ - \sum_k \frac{\langle N_k \rangle}{V} \int d\vec{R}_3 \langle c_{ik}(\vec{R}_1, \vec{R}_3) \rangle \langle h_{kj}(\vec{R}_3, \vec{R}_2) \rangle\end{aligned}\quad (\text{A1-10})$$

And now insert the definition of $\langle h_{kj}(\vec{R}_3, \vec{R}_2) \rangle$ to find

$$\begin{aligned}
 & \langle c_{ij}(\vec{R}_1, \vec{R}_2) \rangle = \frac{1}{\Omega^2} \int d\vec{\Omega}_1 d\vec{\Omega}_2 c_{ij}(1,2) \\
 & + \sum_k \frac{\langle N_k \rangle}{V\Omega^3} \int d\vec{z} d\vec{\Omega}_1 d\vec{\Omega}_2 c_{ik}(1,3) h_{kj}(3,2) \\
 & - \sum_k \frac{\langle N_k \rangle}{V\Omega^2} \int d\vec{z} d\vec{\Omega}_2 \langle c_{ik}(\vec{R}_1, \vec{R}_3) \rangle h_{kj}(3,2)
 \end{aligned} \tag{A1-11}$$

and the terms can be grouped as

$$\begin{aligned}
 & \langle c_{ij}(\vec{R}_1, \vec{R}_2) \rangle - \frac{1}{\Omega} \int d\vec{\Omega}_1 d\vec{\Omega}_2 c_{ij}(1,2) \\
 & = \sum_k \frac{\langle N_k \rangle}{V\Omega^2} \int d\vec{z} d\vec{\Omega}_2 h_{kj}(3,2) \left\{ \frac{1}{\Omega} \int d\Omega_1 c_{ik}(1,3) - \langle c_{ik}(\vec{R}_1, \vec{R}_3) \rangle \right\}
 \end{aligned} \tag{A1-12}$$

Now, use the fact that

$$\langle c_{ij}(\vec{R}_1, \vec{R}_2) \rangle = \frac{1}{\Omega} \int d\Omega_2 \langle c_{ij}(\vec{R}_1, \vec{R}_2) \rangle \tag{A1-13}$$

to rewrite equation A1-12 as

$$\begin{aligned}
 & \frac{1}{\Omega} \int d\Omega_2 \left\{ \langle c_{ij}(\vec{R}_1, \vec{R}_2) \rangle - \frac{1}{\Omega} \int d\vec{\Omega}_1 c_{ij}(1,2) \right\} \\
 & = \sum_k \frac{\langle N_k \rangle}{V\Omega^2} \int d\vec{z} d\vec{\Omega}_2 h_{kj}(3,2) \left\{ \frac{1}{\Omega} \int d\vec{\Omega}_1 c_{ik}(1,3) \right. \\
 & \quad \left. - \langle c_{ik}(\vec{R}_1, \vec{R}_3) \rangle \right\}
 \end{aligned} \tag{A1-14}$$

It is now advantageous to define

$$\kappa_{ij}(\vec{R}_1 \vec{R}_2, \vec{\Omega}_2) = \langle c_{ij}(\vec{R}_1, \vec{R}_2) \rangle - \frac{1}{\Omega} \int d\vec{\Omega}_1 c_{ij}(1, 2) \quad (Al-15)$$

For now equation Al-14 takes the form

$$\begin{aligned} & \frac{1}{\Omega} \int d\Omega_2 \kappa_{ij}(\vec{R}_1, \vec{R}_2, \vec{\Omega}_2) \\ &= \sum_k \frac{\langle N_k \rangle}{V\Omega^2} \int d3d\vec{\Omega}_2 h_{kj}(3, 2) \kappa_{ik}(\vec{R}_1 \vec{R}_3 \vec{\Omega}_3) \end{aligned} \quad (Al-16)$$

and through the use of the identity

$$\begin{aligned} & \kappa_{ij}(\vec{R}_1 \vec{R}_2, \vec{\Omega}_2) \\ &= \sum_k \delta_{jk} \int d3 \kappa_{ik}(R_1 R_3 \Omega_3) \delta(\vec{R}_2 - \vec{R}_3) \delta(\vec{\Omega}_2 - \vec{\Omega}_3) \end{aligned} \quad (Al-17)$$

It is now possible to write the expression for κ_{ij} as

$$\begin{aligned} & \sum_k \frac{\delta_{jk}}{\Omega} \int d3d\vec{\Omega}_2 \kappa_{ik}(R_1 R_3 \Omega_3) \delta(\vec{R}_2 - \vec{R}_3) \delta(\vec{\Omega}_2 - \vec{\Omega}_3) \\ &= - \sum_k \frac{\langle N_k \rangle}{V\Omega^2} \int d3d\Omega_2 h_{kj}(3, 2) \kappa_{ik}(\vec{R}_1 \vec{R}_3 \vec{\Omega}_3) \end{aligned} \quad (Al-18)$$

and this can be rearranged to

$$\left[\frac{1}{\Omega} \int d\vec{3}d\vec{\Omega}_2 \ K_{ik}(\vec{R}_1, \vec{R}_3, \vec{\Omega}_3) \right] \left\{ \delta_{jk} \ \delta(\vec{R}_2 - \vec{R}_3) \ \delta(\vec{\Omega}_2 - \vec{\Omega}_3) \right. \\ \left. + \frac{\langle N_k \rangle}{V\Omega} h_{kj}^{(3,2)} \right\} = 0 \quad (Al-19)$$

The term in brackets is multicomponent density fluctuation functions, which is nonzero almost everywhere (Evans, 1979). And thus a sufficient condition for equation Al-19 to be valid is that

$$K_{ik}(\vec{R}_1, \vec{R}_3, \vec{\Omega}_3) = 0 \quad (Al-20)$$

If this is true, then it is easy to show that

$$\langle \underline{\underline{C}} \rangle = \underline{\underline{C}} \quad (Al-22)$$

which was the desired result.

And thus equation Al-8 can be written as

$$[\underline{\underline{N}} + \underline{\underline{H}}\underline{\underline{H}}\underline{\underline{N}}]^{-1} = [\underline{\underline{N}}^{-1} - \underline{\underline{C}}] \quad (Al-23)$$

APPENDIX 2
 PERTURBATION THEORY FOR DIRECT CORRELATION FUNCTION
 INTEGRALS USING THE RISM THEORY

In Chapter 4 it was noted that theoretical results from perturbation theory can be useful in determining functional forms for empirical models of direct correlation function integrals. An exact result for the direct correlation function perturbations from perturbations in total correlation functions based on the RISM theory is derived below.

The problem considered here is to find the perturbation in $C_{\alpha\beta}$, designated as $C_{\alpha\beta}^1$, that is induced by a change in $h_{\alpha\beta}^0$ from $h_{\alpha\beta}^0$ to $h_{\alpha\beta}^0 + h_{\alpha\beta}^1$. We begin with the Fourier transform of the RISM form of the Ornstein-Zernike equation

$$\hat{h}_{\alpha\beta} = \sum_{\gamma\eta} \hat{\omega}_{\alpha\gamma} \hat{c}_{\omega\eta} \hat{\omega}_{\eta\beta} + \rho_o \sum_{\gamma\eta} \hat{\omega}_{\alpha\gamma} \hat{c}_{\gamma\eta} \hat{h}_{\eta\beta} \quad (A2-1)$$

The caret (^) denotes the Fourier transform and the functions $\hat{\omega}_{\alpha\beta}$ are the transforms of intramolecular correlation functions. We rewrite equation A2-1 in matrix form as

$$\hat{\underline{\underline{H}}} = \hat{\underline{\underline{w}}} \hat{\underline{\underline{C}}} \hat{\underline{\underline{w}}} + \rho_o \hat{\underline{\underline{w}}} \hat{\underline{\underline{C}}} \hat{\underline{\underline{H}}} \quad (A2-2)$$

Equation A2-2 can be rearranged to

$$[\underline{\underline{I}} - \rho_{O \underline{\underline{C}}}^{\hat{\underline{\underline{C}}}}][\underline{\underline{I}} + \rho_{O \underline{\underline{H}}}^{\hat{\underline{\underline{H}}}^{-1}}] = \underline{\underline{I}} \quad (A2-3)$$

where $\underline{\underline{I}}$ is an identity matrix. The terms in the matrix $\underline{\underline{H}}$ are split into reference contributions ($\underline{\underline{H}}^0$) and perturbation contributions ($\underline{\underline{H}}^1$) where the $\underline{\underline{H}}^0$ are assumed to obey an equation like A2-3 with a matrix of reference contributions to the direct correlation functions ($\underline{\underline{C}}^0$). We wish to determine the perturbation induced in the direct correlation functions ($\underline{\underline{C}}^1$) defined by

$$\underline{\underline{C}}^1 = \underline{\underline{C}} - \underline{\underline{C}}_0 \quad (A2-4)$$

Use of a mathematical identity leads to

$$\begin{aligned} [\underline{\underline{I}} - \rho_{O \underline{\underline{C}}}^{\hat{\underline{\underline{C}}}}] &= [\underline{\underline{I}} + \rho_{O \underline{\underline{H}}}^{\hat{\underline{\underline{H}}}^0 \hat{\underline{\underline{C}}}^{-1}}] - [\underline{\underline{I}} + \rho_{O \underline{\underline{H}}}^{\hat{\underline{\underline{H}}}^0 \hat{\underline{\underline{C}}}^{-1}}] \rho_{O \underline{\underline{H}}}^{\hat{\underline{\underline{H}}}^1 \hat{\underline{\underline{C}}}^{-1}} \\ &\quad * [\underline{\underline{I}} - \rho_{O \underline{\underline{C}}}^{\hat{\underline{\underline{C}}}}] \end{aligned} \quad (A2-5)$$

Solution for $\underline{\underline{C}}^1$ gives

$$\begin{aligned} \rho_{O \underline{\underline{C}}}^{\hat{\underline{\underline{C}}}^1} &= [\underline{\underline{I}} + (\underline{\underline{I}} - \rho_{O \underline{\underline{C}}}^{\hat{\underline{\underline{C}}^0}}) \rho_{O \underline{\underline{H}}}^{\hat{\underline{\underline{H}}}^1 \hat{\underline{\underline{C}}}^{-1}}] \\ &\quad [(\underline{\underline{I}} - \rho_{O \underline{\underline{C}}}^{\hat{\underline{\underline{C}}^0}}) \rho_{O \underline{\underline{H}}}^{\hat{\underline{\underline{H}}}^1 \hat{\underline{\underline{C}}}^{-1}} (\underline{\underline{I}} - \rho_{O \underline{\underline{C}}}^{\hat{\underline{\underline{C}}^0}})] \end{aligned} \quad (A2-6)$$

This result is formidable, but exact. It can be expanded in powers of $\underline{\underline{H}}^1$ to yield

$$\begin{aligned} \hat{\underline{\underline{\omega}}}^{-1}_1 &= \hat{\underline{\underline{H}}}^{-1}\hat{\underline{\underline{\omega}}}^{-1} - \rho_0 \hat{\underline{\underline{H}}}^{-1}\hat{\underline{\underline{\omega}}}^{-1}\hat{\underline{\underline{\omega}}}^{-1}_0 - \rho_0 \hat{\underline{\underline{\omega}}}^{-1}\hat{\underline{\underline{H}}}^{-1}\hat{\underline{\underline{\omega}}}^{-1} \\ &\quad + \rho_0^2 \hat{\underline{\underline{\omega}}}^{-1}_0\hat{\underline{\underline{H}}}^{-1}\hat{\underline{\underline{\omega}}}^{-1}\hat{\underline{\underline{\omega}}}^{-1}_0 + O[(\hat{\underline{\underline{H}}}^{-1})^2] \end{aligned} \quad (A2-7)$$

This result is still difficult to use. However, the low density limit is given by

$$\hat{\underline{\underline{\omega}}}^{-1}\hat{\underline{\underline{\omega}}} = \rho_0 \lim_{\alpha \rightarrow 0} \hat{\underline{\underline{H}}}^{-1} \quad (A2-8)$$

This is a RISM form of the mean spherical approximation. In the low density limit we have

$$\hat{h}_{\alpha\beta} = \int d\mathbf{l} d\mathbf{d} 2 d\vec{r} \delta(\vec{r}_1^\alpha) \delta(\vec{r}_2^\gamma - \vec{r}) f(1,2) e^{-\vec{k} \cdot \vec{r}} \quad (A2-9)$$

where $f(1,2) = C^{-\beta u(1,2)} - 1$ and $u(1,2)$ is the intermolecular pair potential. If u is split into reference and perturbation terms, we find that

$$\hat{h}_{\alpha\beta}^{-1} = \int d\mathbf{l} d\mathbf{d} 2 d\vec{r} \delta(\vec{r}_1^\alpha) \delta(\vec{r}_2^\gamma - \vec{r}) C^{-\beta u^0(1,2)} f^1(1,2) e^{-\vec{k} \cdot \vec{r}} \quad (A2-10)$$

If the reference system is a hard sphere, or hard core, system, then the result in equation A2-10 simplifies to

$$\hat{h}_{\alpha\gamma}^{-1} = \int d\mathbf{l} d\mathbf{d} 2 \delta(\vec{r}_1^\alpha) \delta(\vec{r}_2^\gamma - \vec{r}) f^1(1,2) e^{-\vec{k} \cdot \vec{r}} \quad (A2-11)$$

If the intermolecular perturbation potential is written as a sum of group-group terms

$$u^1(1,2) = \sum_{\eta\lambda} u_{\eta\lambda}^1 (\vec{r}_1^\eta - \vec{r}_2^\lambda) \quad (A2-12)$$

Then the elements of the $\underline{\underline{H}}^1$ matrix can be found as

$$\underline{\underline{H}}^1 = \sum_{n=1}^{\infty} (\hat{\omega}(-\beta \underline{\underline{u}}^1)) \frac{n}{n!} \quad (A2-13)$$

This allows for identification of the perturbation in the direct correlation function as

$$\underline{\underline{C}}^1 = -\beta \underline{\underline{u}}^1 + \beta^2 \underline{\underline{\omega}}^1 \frac{\hat{\omega}}{2!} - \beta^3 \underline{\underline{\omega}}^1 \underline{\underline{\omega}}^1 \frac{\hat{\omega}}{3!} + \dots \quad (A2-14)$$

And then, at a macroscopic level ($k \rightarrow 0$) this suggests that

$$c_{\alpha\beta}^1 = a_{\alpha\gamma} + \beta_{\alpha\gamma}/T + c_{\alpha\beta}/T^2 + \dots \quad (A2-15)$$

The perturbation should be an expansion in powers of $1/T$. This form is utilized in this work.

APPENDIX 3
THREE BODY DIRECTION CORRELATION FUNCTION INTEGRALS

It is possible to define a hierarchy of direct correlation functions and their integrals for any number of molecules. In specific, the three body direct correlation function integrations are

$$c_{ijk} = \left(\frac{\partial c_{ij}}{\partial \rho_k} \right)_{T, \rho_{\ell \neq k}} \quad (A3-1)$$

If the two body direct correlation function integral is represented using the RISM theory

$$c_{ij} = \sum_{\alpha \beta} v_{i\alpha} v_{j\beta} c_{\alpha \beta} \quad (A3-1.5)$$

Then the total differential of this function, at constant temperature, is

$$dc_{ij} = \sum_{\alpha \beta \gamma} v_{i\alpha} v_{j\beta} \left(\frac{\partial c_{\alpha \beta}}{\partial \rho_{\gamma}} \right)_{T, \rho_{\delta \neq \gamma}} d_{\rho_{\gamma}} \quad (A3-2)$$

When a three site direct correlation function integral is defined in a manner analogous to equation A3-1, then a relationship between the molecular and site three body functions is obtained

$$c_{ijk} = \sum_{\alpha\beta\gamma} v_{i\alpha} v_{j\beta} v_{k\gamma} c_{\alpha\beta} \left(\frac{\partial \rho}{\partial \rho_k} \right)_{\rho_\ell} \quad (A3-3)$$

and the use of the material balance then leads to

$$c_{ijk} = \sum_{\alpha\beta\gamma} v_{i\alpha} v_{j\beta} v_{k\gamma} c_{\alpha\beta\gamma} \quad (A3-4)$$

This simple relationship shows how the RISM approximation can be extended to multibody correlation functions. It is obvious that this technique can be extended ad nauseam to form group contribution theories for higher-order correlation functions.

APPENDIX 4 NONSPHERICITY EFFECTS

Experimental data presented in Chapter 5 (that was used to develop figures 5-1 and 5-2) show that, for dense liquids, a two-parameter corresponding states relationship exists as

$$\frac{\partial P\beta}{\partial \rho} = f(\tilde{\rho}, \tilde{T}) \quad (\text{A4-1})$$

This would be expected for simple molecules with spherically symmetric potential functions. The fact that this same correlation can apply to simple molecules (Ar), long chain molecules (normal hexadecane) and polar species (ammonia) is somewhat surprising. This appendix offers justification for this type of correlation using both microscopic and macroscopic agreements.

General Considerations

The intermolecular potential determines the state of a system for a given density and temperature in the absence of external fields. The actual force that acts on any molecule is dependent on the phase space coordinates of all other molecules in the system.

For simplicity these initial considerations will be discussed in terms of a symmetric pair potential. For many molecules this is similar to that shown in Figure A4-1. For intermolecular separations less than r_a the interaction is repulsive, and the interaction is attractive for greater separations. For dense fluids the typical intermolecular separation is less than r_a so that the dominant forces are repulsive. For low pressure gases the typical separation is of the magnitude of r_b or larger. Then the dominant type of interaction is attractive.

This is surely a simplified picture of reality because for real molecules the orientations must be considered. There are both short-ranged and long-ranged forces of the attractive and repulsive forms. However, this suggests the proper form to follow for the analysis. There are two separate contributions to consider:

1. Molecular shape--the short range repulsive forces should depend on the shape of the molecule.
2. Long-range anisotropic forces--multiple moments are of long range and depend on molecular orientation.

Molecular Shape Effects

For dense fluids the molecules are tightly packed. The packing is determined by the harshly repulsive part of intermolecular potential. For nonspherical molecules these effects must be shape dependent. Barker and Henderson (1981) and Steele and Sandler (1974) have shown that harshly

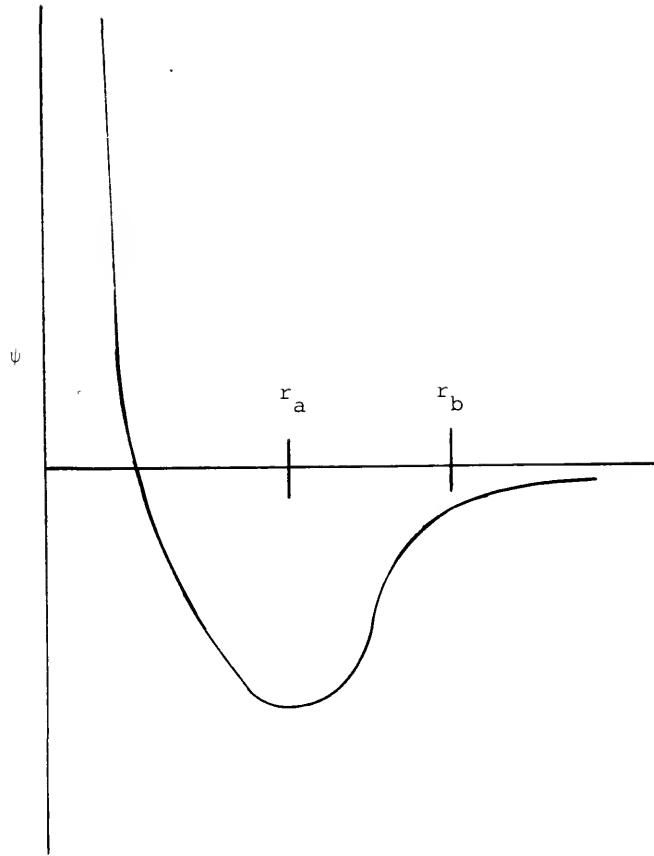


Figure A4-1. Typical intermolecular potential.

repulsive potentials can be modeled as hard core potentials if the core size is taken as temperature dependent. The analysis here will then be to compare hard sphere systems with general hard body systems.

A general hard body theory does not exist. The properties of hard convex bodies have been determined using the scaled particle theory (Gibbons, 1970) and an extension of the Carnahan-Starling theory (Boublik, 1974). Rigby (1976) has shown that it is possible to calculate the properties of concave bodies using the convex body equations if the parameters are properly selected.

Two points are to be addressed here. First, can general convex bodies be represented as spheres? An affirmative answer to this question could explain, to a large degree, the existence of the corresponding states principle for the dense fluids. A second question to consider is will the proposed theory, that for overlapping spheres, give a better representation of the molecular properties than the spherical model.

For hard convex bodies Boublik (1974) has presented what seems to be the most accurate expression (Boublik, 1975). For a pure component this is

$$z = \frac{1+(3\gamma-2)y+(3\gamma^2-3+1)y^2-\gamma^2y^3}{(1-y)^3} \quad (\text{A4-2})$$

where

$$y = \rho V$$

V = molecule volume

γ is a single parameter that represents the non-sphericity.

For hard spheres $\gamma = 1$ and equation A4-2 reduces to that of Carnahan and Starling. To determine the ability of the hard sphere equation to represent the hard convex bodies, for calculation of pressure changes, the problem is formulated by realizing that in general from equation A4-2 we have

$$\frac{\partial P_B}{\partial \rho} = f(y, \gamma) \quad (A4-3)$$

An equivalent hard sphere size was found that minimized sum squared errors in pressure deviations calculated over the dense fluid range. The following variational problem was solved:

Find a such that

$$I = \int_{\rho_{\min}}^{\rho_{\max}} [f(y, \gamma) - f(ay, 1)]^2 d\rho \quad (A4-4)$$

was a minimum. The value of a was found to be sensitive to the density range evaluated but the following values were used as representative.

$$\rho_{\min} = 0.2/V \quad (A4-5a)$$

$$\rho_{\max} = 0.6/V \quad (\text{A4-5b})$$

The value of α was found to be a smooth function of γ for values of γ from 1 to 3. $\gamma = 3$ would correspond to a spherocylinder with a length to diameter ratio of about 10. Figure A4-2 shows the comparison for a spherocylinder system using these results. Notice that the agreement is not exact. The equivalent hard sphere is always one with a volume larger than that of the convex body. If the differences are analyzed, it can be shown that the form

$$\left. \frac{\partial \rho \beta}{\partial P} \right|_{CB} = \left. \frac{\partial P \beta}{\partial \rho} \right|_{EHS} + c\rho \quad (\text{A4-6})$$

yields excellent agreement, where the superscripts are CB for convex body and EHS for equivalent hard sphere. This may explain much of the success that Mathias (1979) had in his correlation of dense fluid properties.

The question of whether the RISM approximation employed in this work can yield good agreement for hard body systems is more difficult to answer due to lack of data. The direct correlation values given by Lowden and Chandler (1973) for a hard diatomic system have been integrated to yield the thermodynamic derivations. These are shown in Figure A4-3. Chen and Steele (1971) have solved the Ornstein-Zernike equation for this same system using a Percus-Yevick approximation.

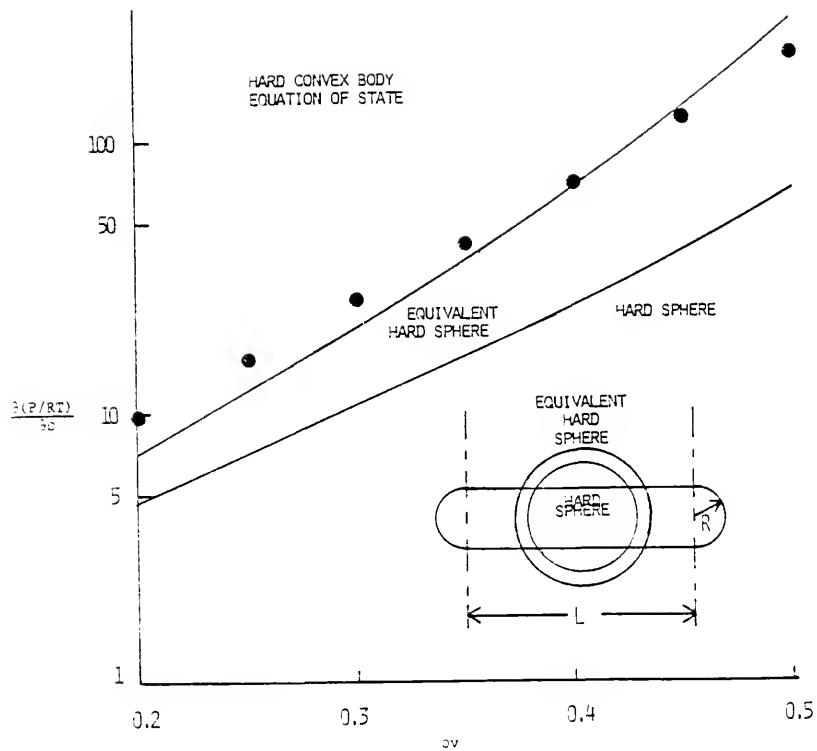


Figure A4-2. Dimensionless compressibility versus dimensionless density for hard core systems.

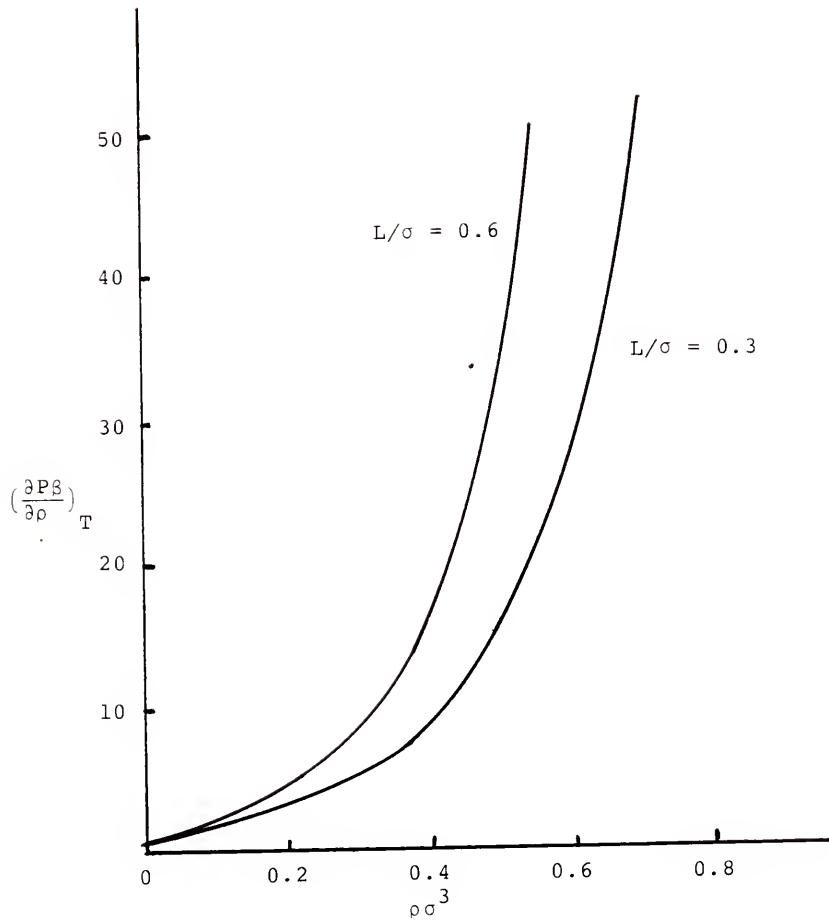


Figure A4-3. Dimensionless compressibility versus density for homonuclear diatomics calculated using RISM direct correlation functions.

A comparison of these results is shown in Figure A4-4. The RISM theory offers a good approximation. It should be noted that Chen and Steele's results came from the compressibility relation using the P-Y approximation. Thus, they would be expected to overestimate the exact result for a diatomic. This then offers even greater hope for the RISM theory. Figure 4-2 in Chapter 4 also shows a comparison of the RISM result for this system with results from Monte Carlo calculations; again the comparison is favorable.

These results suggest that the RISM formulation should be more accurate for the representation of the hard core system than use of a spherical reference, but that if properly formulated, the spherical systems can also work well.

Effects of Long Range Interactions

For polar molecules the effects of the multipole moments on thermodynamic properties can be large in the vapor phase. However, in the liquid phase the harsh repulsive forces seem to dominate. A prime example of this behavior is shown in Figure A4-5 for argon and water. The reducing parameters for water were chosen to yield the optimum correspondence for these two substances. It can be seen that these two different fluids behave similarly in the dense fluid region while being highly dissimilar in the vapor region.

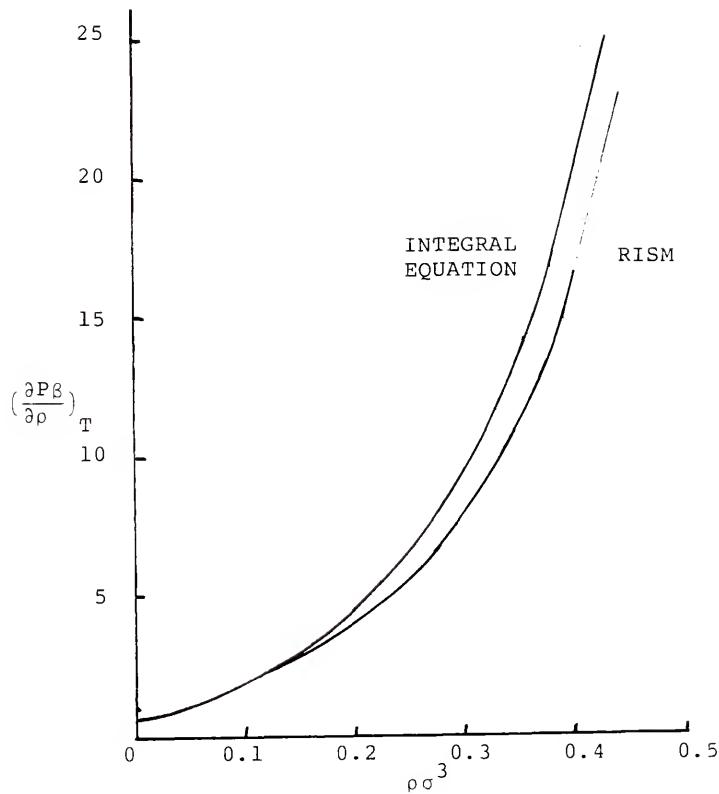


Figure A4-4. Comparison of RISM and integral equation results for homonuclear diatomics with $L/\sigma = 0.6$.

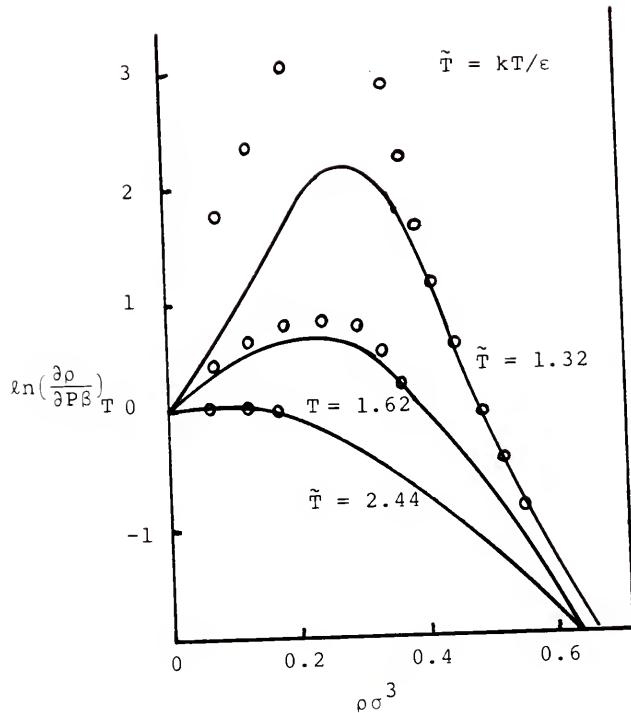


Figure A4-5. Comparison of the Bulk Modulus for Argon (lines) and water (o). ϵ and σ for argon are from virial coefficient calculations and ϵ and σ for water were determined for best correspondence.

Gubbins and O'Connell (1974) have analyzed this behavior for multipolar potentials and spherical molecules. They find

$$\frac{\partial P\beta}{\partial \rho} \approx \left. \frac{\partial P\beta}{\partial \rho} \right|_o [1 - G_\chi / \left. [\partial P\beta / \partial \rho] \right|_o] \quad (A4-7)$$

where the subscript o represents the properties of a spherical reference system. Using a Lennard-Jones reference system the quantity G was found to be approximately -1 for a dipolar interaction. In the dense fluid state $\frac{\partial P\beta}{\partial \rho} \approx 0.05$ so that the anisotropic forces contribute approximately 5% to the value of $\partial P\beta / \partial \rho$. This suggests that a low order perturbation expansion, as used in this work, should be adequate.

Summary

This appendix has been dedicated to a study of nonsphericity effects on thermodynamic properties. Two separate considerations were examined--the shape of the molecule and anisotropic long-range forces. It was shown that the nonspherical shape could be adequately represented using the RISM theory or even with the properly chosen spherical reference. The anisotropic forces can be a noticeable effect but the low order perturbations should be adequate for the systems of interest.

APPENDIX 5 HARD SPHERE PROPERTIES

Exact expressions for the correlation functions and thermodynamic properties of hard sphere mixtures are not available. However, good approximate results can be obtained using the Percus-Yevick approximation. Certain aspects of this approximation and its ramifications on the form of the hard sphere equation of state are developed below.

To determine the properties of any system of molecules, one begins the analysis with the Ornstein-Zernike (1914) equation

$$h_{ij}(\vec{r}) = c_{ij}(\vec{r}) + \sum_k \rho_k \int d\vec{s} c_{ik}(\vec{r}-\vec{s}) h_{kj}(\vec{s}) \quad (A5-1)$$

The form of the Ornstein-Zernike equation is valid for any system of molecules, acting with spherically symmetric intermolecular potentials, not in an external field. This represents a set of $N(N+1)/2$ coupled integral equations that contain $N(N+1)$ unknown functions, for an N component system. For a mixture of hard spheres there are a complementary set of exact conditions

$$h_{ij}(\vec{r}) = -1 \quad \text{for } |\vec{r}| < \sigma_{ij} \quad (A5-2)$$

which represent the impenetrability of the hard cores.

For the cases of interest the characteristic length σ_{ij} is given by

$$\sigma_{ij} = \frac{1}{2} (\sigma_i + \sigma_j) \quad (A5-3)$$

where σ_i is the diameter of molecule i. Percus and Yevick (1958) have proposed a set of approximate closure relations for the direct correlation functions that when combined with equations A5-1 and A5-2 yield a set of equations that can be solved for the direct correlation functions and the equation of state. These approximate relations for a hard sphere system are

$$c_{ij}(\vec{r}) = 0 \quad \text{for } |\vec{r}| > \sigma_{ij} \quad (A5-4)$$

Wertheim (1963) and Thiele (1963) offered, independently, solutions to this problem for pure components. Later, Lebowitz (1964) gave the solution for a binary mixture. Baxter (1970) has shown an elegant approach for the solution for multicomponent systems.

Once the correlation functions are known for the hard sphere, the equation of state can be determined in two obvious ways. The so-called compressibility result is found from

$$\left(\frac{\partial P\beta}{\partial \rho}\right)_{T,\underline{X}} = 1 - \sum_i \chi_i \rho_j \int d\vec{r} c_{ij}(\vec{r}) \quad (A5-5)$$

with use made of the ideal gas limit to express this as a complete equation of state. The other form of equation of state, known as the virial results, is found from the virial theorem

$$P\beta = \rho - \left(\frac{2}{3}\right) \pi \sum_{ij} \rho_i \rho_j \int_0^\infty dr r^3 \left(\frac{d\psi_{ij}}{dr}\right) \sigma_{ij}(r) \quad (A5-6)$$

Another, more roundabout, approach to obtain an equation of state is possible. One may first obtain the internal energy and then use thermodynamic identities to find the pressure.

Because the correlation functions determined with use of the Percus-Yevick approximation are not exact, the different routes to the equation of state all yield different results. For pure components the closed form results available are

$$\text{Compressibility: } z = (1+n+n^2)/(1-n)^3 \quad (A5-7a)$$

$$\text{Virial: } z = (1+n+n^2-3n^3)/(1-n)^3 \quad (A5-7b)$$

where n , the packing fraction, is found as

$$\eta = \left(\frac{1}{6}\right)\pi\rho\sigma^3$$

These results are known to be upper (compressibility) and lower (virial) bounds to the exact hard sphere results as determined from computer simulation (Reed and Gubbins, 1973).

By comparison of the density series expansions of the exact and approximate results for pure hard spheres Carnahan and Starling (1969) developed an expression which very accurately represents the hard sphere equation of state

$$z = (1+\eta+\eta^2-\eta^3)/(1-\eta)^3 \quad (\text{A5-8})$$

A generalization of all of these results can be written as

$$z = (1+\eta+\eta^2+\alpha\eta^3)/(1-\eta)^3 \quad (\text{A5-9})$$

where different values of the parameters α can yield any of the aforementioned forms.

There are several ways that a value of α could be chosen. One reasonable approach would be to use α to match the known virial coefficients for hard sphere fluids. Table A5-1 shows the values of α required to reproduce the known

TABLE A5-1

VALUES OF α^a (EQUATION A5-9) REQUIRED TO MATCH KNOWN^b
VIRIAL COEFFICIENTS FOR HARD SPHERES

Virial Coefficient	α
4th	-0.6384
5th	-0.9211 \pm 0.0256
6th	-1.0789 \pm 0.0683
7th	-0.7475 \pm 0.1638

^aThe second and third virial coefficients are independent of α .

^bThe fourth virial coefficient is evaluated exactly, whereas the fifth and higher virial coefficients have been determined using Monte Carlo integration, and the errors indicated are based on the statistical error of those calculations.

virial coefficients (Hansen and McDonald, 1976) for hard spheres. These results show that the Carnahan-Starling equation (A5-8), for which $\alpha = -1$, gives a reasonable approximation for the known virial coefficients. In this work α will be treated as a parameter determined through analysis of experimental data as described in Chapter 5.

An important consideration in the choice of a value for α is that the hard sphere systems show no vapor-liquid phase transition. This implies that

$$\frac{dz^{HS}}{dn} > 0 \quad 0 < n < 1 \quad (A5-10)$$

Using equation (A5-9) it is possible to predict a maximum in Z for certain values of α . This is actually the case for all negative values of α . The location of the maximum in Z^{HS} is given by

$$n^{\max} = \frac{-\beta \pm \sqrt{\beta^2 - 4\beta}}{2} \quad (A5-11)$$

with β determined as

$$\beta = 4/(3\alpha + 1) \quad (A5-12)$$

Analysis of these results shows that any value of α less than -3 will yield a maximum in Z^{HS} for values of n less than 1. However, on a purely physical basis n

should never exceed that for closest packing of spheres which is approximately 0.74. For the value of α used in this work, -4.2, equation A5-9 will show a maximum in the compressibility factor at n equal to 0.784. Thus, these results should probably not be used for n values greater than 0.75.

To extend these results to mixtures α can be treated as a constant that acts as an interpolating parameter between the compressibility theorem (denoted as PYC) and virial theorem (denoted as PYV) results. The, compressibility factors and chemical potentials are found using

$$z^{\text{HS}} = z^{\text{PYC}} + \left(\frac{\alpha}{3}\right) [z^{\text{PYC}} - z^{\text{PYV}}] \quad (\text{A5-13a})$$

$$\beta\mu_i^{\text{HS}} = \beta\mu_i^{\text{PYC}} + \left(\frac{\alpha}{3}\right) [\beta\mu_i^{\text{PYC}} - \beta\mu_I^{\text{PYC}}] \quad (\text{A5-13b})$$

The complete expressions for all of the required quantities are

$$z^{\text{PYC}} = \frac{1}{\xi_0} \left[\frac{\xi_0}{1-\xi_3} + \frac{3\xi_1\xi_2}{(1-\xi_3)^2} + \frac{3\xi_2^3}{(1-\xi_3)^3} \right] \quad (\text{A5-14a})$$

$$z^{\text{PYC}} - z^{\text{PYV}} = \frac{3\xi_3\xi_2^3}{\xi_0(1-\xi_3)^3} \quad (\text{A5-14b})$$

$$\begin{aligned} \beta\mu_i^{\text{PYC}} = & \beta\mu_i' - \ln(1-\xi_3) + \sigma_i^3 \xi_0 z^{\text{PYC}} \\ & + \frac{3\sigma_i \xi_2}{(1-\xi_3)} + \frac{3\sigma_i^2 \xi_1}{(1-\xi_3)} + \frac{9\sigma_i^2 \xi_2^2}{2(1-\xi_3)^2} \end{aligned} \quad (\text{A5-14c})$$

$$\begin{aligned}
 [\beta \mu_i^{PYC} - \beta \mu_i^{PYV}] &= \frac{\sigma_i^2 \xi_2}{\xi_3^2} \ln(1-\xi_3) [3\xi_2^2 \sigma_i - 1/2] \\
 &+ \frac{3\sigma_i^3 \xi_2^3}{2(1-\xi_3)^3} [6 + \frac{2(1-\xi_3)}{\xi_3^2} - \frac{4(1-\xi_3)}{\xi_3} + \frac{(1-\xi_3)^2}{\xi_3^2}] \\
 &+ \frac{3\sigma_i^2 \xi_2}{2(1-\xi_3)^2} [9 - \frac{6}{\xi_3}]
 \end{aligned} \tag{A5-14d}$$

where

$$\xi_\ell = \frac{\pi}{6} \sum_i \rho_i \sigma_i^\ell \tag{A5-14e}$$

APPENDIX 6
COMPUTER PROGRAMS

AUGUST 26, 1981

11:29

NEROC -- SYSTEM SUPPORT UTILITIES --

C PROGRAM HARD SPHERE

C THIS IS DESIGNED TO BE A MULTIPURPOSE PROGRAM FOR
C FITTING DATA TO THE PERTURBED HARD SPHERE FORM
C PROPOSED FOR THE DIRECT CORRELATION FUNCTION INTEGRALS
C THERE ARE TWO GENERAL OPTIONS AVAILABLE TO THE USER
C NOPT=1---HERE THE INPUT DATA IS THE TYPE OF HARD SPHERE
C EQUATION TO BE USED AND THEN ISOTHERMAL SETS
C OF VOLUME AND OCFI DATA AND A VALUE OF THE HARD
C SPHERE DIAMETER(DIMENSIONLESS) FOR THE ISOTHERM
C THE PROGRAM WILL CALCULATE THE HARD SPHERE OCFI
C AND THE CORRESPONDING VIRIAL COEFFICIENT
C NOPT=2---WITH THIS OPTION AN OPTIMAL VALUE OF THE
C HARD SPHERE DIAMETER WILL BE FOUND FOR AN
C ISOTHERM BY MINIMIZING THE SUM SQUARED
C DEVIATIONS OF THE VIRIAL COEFFICIENTS FROM
C THE MEAN ALONG THE ISOTHERM
C AGAIN SEVERAL FORMS OF HARD SPHERE EQUATION
C OF STATE ARE AVAILABLE

C THE INPUT DATA IS SLIGHTLY DIFFERENT FOR THE DIFFERENT
C OPTIONS. IN BOTH CASES THE FIRST CARD SHOULD CONTAIN THE
C COMPONENT NAME AND CRITICAL PROPERTIES. THE NEXT CARD
C CONTAINS THE VALUE OF THE PARAMETER ALPHA THAT DETERMINES
C THE TYPE OF HARD SPHERE EQUATION USED.

ALPHA	EQUATION
0	PYC
-3	PYV
-1	CS
-3 TO -1	SOFTER THAN CS
-1 TO 0	HARDER THAN CS

C THE NEXT CARD CONTAINS NOPT =1 FOR CALCULATION AND
C =2 FOR REGRESSION

C NEXT CARD IS THE FIRST TEMPERATURE

C ENTER 0 IF THE END OF AN ISOTHERM

C ENTER NUMBER LARGER THAN 10**4 FOR A NEW COMPONENT

C THEN SETS OF V AND C EIGHT TO A CARD

C FINALLY IF NOPT =1 ENTER XMAX,XMIN AND XINT

C IF NOPT=2 ENTER INITIAL GUESS FOR X

C ALL CALCULATIONS IN DOUBLE PRECISION

IMPLICIT REAL*8 (A-H,O-Z)

DIMENSION VI(2),CI(8),FOL(10),INA(3),V(30),C(30),DEL(30),

* E(30),NAME(5),CHS(30),A(7)

```
C RESTRICTED TO 30 POINTS ON AN ISOTHERM
COMMON /TITLE/ NAME,TC,VC
COMMON /WRITER/ NOPT
C ENTER NAME AND CRITICAL PROPERTIES
100 READ(5,1,END=9999)NAME,TC,VC
1 FORMAT(5A4,2F10.0)
C WRITE HEADER AND THEN ECHO NAME AND TC AND VC
  WRITE(6,2)
2 FORMAT(10X,'ANALYSIS OF DIRECT CORRELATION FUNCTION'
*,* MODEL USING HARD SPHERE REFERENCE SYSTEM',///)
  WRITE(6,3)NAME,TC,VC
3 FORMAT(10X,'DATA FOR ',5A4,///,10X,'CRITICAL PROPERTIES',
* ,10X,'CRITICAL TEMPERATURE =',F5.3,'K',/,10X,
* 'CRITICAL VOLUME =',F9.4,'CC/MOLE',///)
C ENTER OPTION FOR CALCULATION OR REGRESSION
READ(5,6)NCPT
6 FORMAT(12)
C ECHO TYPE OF CALCULATION PERFORMED
  GO TO (1000,2000),NCPT
1000 WRITE(6,7)
7 FORMAT(10X,'PROGRAM IN CALCULATIONAL MODE',///).
  GO TO 3000
2000 WRITE(6,8)
3 FORMAT(10X,'PROGRAM IN REGRESSION MODE',///)
C SET COUNTER FOR NUMBER OF DATA POINTS ON AN ISOTHERM
3000 NP=0
C TOL USED TO DECIDE IF A NEW ISOTHERM IS ENCOUNTERED
  TOL=0.000
```

AUGUST 26, 1981 11:29 NERDC -- SYSTEM SUPPORT UTILITIES --

```

C      ENTER THE TEMPERATURE
200  READ(5,4)T
4      FORMAT(F10.0)
C      CHECK TO SEE IF THE END OF AN SETHERM
IF(T.LT.1.000) GO TO 400
C      CHECK TO SEE IF END OF A COMPONENT DATA SET
IF(T.GT.1.000) GO TO 100
C      INPUT VOLUME AND DCFI
READ(5,9)V1,CI
9      FORMAT(8F10.0)
C      CHECK TO SEE IF A NEW ISOTHERM
IF(NP.EQ.0) GO TO 300
IF(DABS(T-TOLD).GT.0.5D0) NP=0
C      NOW PACK DATA FOR THE ISOTHERM AND CALCULATE NP
300  DO 10 I=1,E
     IF(V1(I).LT.1.000) GO TO 10
     NP=NP+1
     V(NP)=V1(I)
     C(NP)=CI(I)
10    CONTINUE
     TOLD=T
C      RETURN FOR NEXT ISOTHERM
     GO TO 200
C      DECIDE WHAT TO READ NEXT
400  GO TO (11,12),NCFT
11   READ(5,101)XMAX,XMIN,XINT
101  FORMAT(3F10.0)
102  READ(5,105)NA,A
105  FORMAT(I2,EX.7F10.0)
     DO 20 K=1,NA
     AL=A(K)
     WRITE(6,5)AL
5      FORMAT(10X,'VALUE OF ALPHA IS',FB.2//,10X,
*      'ALPHA=0 IS PYC',//,10X,'ALPHA=-3 IS PYV',//,10X,
*      'ALPHA=-1 IS CS',//)
C      CALCULATE NUMBER OF VALUES OF X TO BE TRIED
     NX=1+(XMAX-XMIN)/XINT
C      BEGIN CALCULATIONS FOR DIFFERENT X VALUES
     DO 20 J=1,NX
     X=XMIN+XINT*DFLOAT(J-1)
     CALL FUN(C,V,AL,X,F,VC,NP,CHS,E,DEL)
     CALL OUT(X,C,V,F,TOLD,NP,CHS,E,DEL)
20    CONTINUE
C      RETURN FOR NEW ISOTHERM

```

```
      GC TO 200
C     READ DATA FOR REGRESSION
12    READ(5,4)X
      READ(5,105)NA,A
      DO 50 K=1,NA
      AL=A(K)
      WRITE(6,5)AL
      WRITE(6,12)X
126   FCFMAT(10X,'INITIAL GUESS OF X =',F12.5,///)
C     BEGIN REGRESSION USING RQUADD
      ITEST=2
2100  CALL RQUADD(ITEST,X,F,100,1.0D-6,1.0D-6,0.1D0,RDL,INA)
      GU TO (1100,1200,1300),ITEST
C     EVALUATION OF SSC
1100  CALL FUN(C,V,AL,X,F,VC,NP,CHS,E,DEL)
      GO TO 2100
C     REGRESSION COMPLETE--PRINT RESULTS
1200  CALL OUT(X,C,V,F,TOLD,NP,CHS,E,DEL)
C     RETURN FOR NEW ISOTHERM
      GC TO 50
C     ERROR IN REGRESSION
1300  CALL ERRDP(X,F,ITEST,TCLD)
C     RETURN FOR NEW TEMPERATURE
50    CONTINUE
      GC TO 200
5555  STOP
      END
      SUBROUTINE CALC(AL,X,V,E,CHS,VC)
```

AUGUST 26, 1981

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NERDC -- SYSTEM SUPPORT UTILITIES --

```
C THIS ROUTINE CALCULATES THE DCFI FOR THE GENERAL HARD
C SPHERE EQUATION OF STATE
C ALL CALCULATIONS IN DOUBLE PRECISION
IMPLICIT REAL*8 (A-H,O-Z)
C CALCULATE THE PACKING FRACTION AND DCFI
E=X*VC/V
CHS=(1.0D0+AL)*E**4-4.0D0*(1.0D0+AL)*E**3+2.0D0*E**2-
* 8.0D0*E)/(1.0D0-E)**4
RETURN
ENC
SUBROUTINE FUN(C,V,AL,X,F,VC,NP,CHS,E,DEL)
C THIS SUBROUTINE CALLS CALC TO EVALUATE THE HSDCFI FOR
C THE VALUE OF X SENT FROM RQUADC AND THEN FINDS THE
C VIRIAL TERMS FOR EACH DENSITY AND AVERAGES. THE
C OUTPUT IS THE SUM SQUARED DEVIATIONS FROM THIS MEAN
C ALL CALCULATIONS IN DOUBLE PRECISION
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION C(1),V(1),CHS(1),E(1),DEL(1)
COMMON /AVG/DMEAN
C INITIALIZE MEAN TO ZERO
DE=0.0D0
DO 10 I=1,NP
CALL CALC(AL,X,V(I),E(I),CHS(I),VC)
DEL(I)=(C(I)-CHS(I))*V(I)
10 DB=DB+DEL(I)
C FIND AVERAGE
DMEAN=DB/NP
C INITIALIZE SSD TO 0
F=0.0D0
DO 20 I=1,NP
F1=(DEL(I)-DMEAN)**2
20 F=F+F1/V(I)
RETURN
ENC
SUBROUTINE CLT (X,C,V,F,T,NP,CHS,E,DEL)
C THIS SUBROUTINE IS USED TO PROVIDE OUTPUT FROM THE
C REGRESSION MODE OF HARD SPHERE
C NO CALCULATIONS ARE PERFORMED
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION C(1),V(1),CHS(1),E(1),DEL(1),NAME(5)
COMMON /AVG/DMEAN
COMMON /TITLE/ NAME,TC,VC
COMMON /WRITER/ NOPT
C CALCULATE AND OUTPUT THE REDUCED TEMPERATURE
```

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```
4 FORMAT(10X,F2.3,2X,F7.4,2X,F7.4,2X,F8.3,2X,F8.3,2X,F10.4,
* 2X,F8.3,2X,F15.4)
3=S/NP
WRITE(6,5)
5 FORMAT(10X,'AVERAGE ABSOLUTE DEVIATION IN C IS ',F10.4,///)
RETURN
END
SUBROUTINE ERROR(X,F,I,T)
THIS SUBROUTINE WILL PRINT ERROR MESSAGES RESULTING
FROM PROBLEMS ENCOUNTERED IN RQUADD
IMPLICIT REAL*8 (A-H,O-Z)
I=I-2
GO TO (1,2),!
1 WRITE(6,3)T,X,F
3 FORMAT(10X,'ERROR IN RQUADD DUE TO ROUNDOFF',///,10X,
* 'TEMPERATURE = ',F12.4,/,10X,'LAST VALUE OF X = ',F12.4,
* //,10X,'FUNCTION = ',D15.5,///)
RETURN
2 WRITE(6,4)T,X,F
4 FORMAT(10X,'ERROR---TOO MANY ITERATIONS AT T=',F12.5,/,
* 10X,'VALUE OF X IS ',F12.4,2X,'WITH F = ',D15.5,///)
RETURN
END

END OF FILE ON SYSIN.
```

```

TR=T/TC
1  WRITE(6,1)T,TR
FORMAT(10X,'TEMPERATURE =',F9.3,5X,'T/TC =',F10.4,///)
C  OUTPUT HARD SPHERE DIAMETER,AVERAGE VIRIAL COEFFICIENT AND
C  SUM SQUARED DEVIATION
C  SUM SQUARED DEVIATION
GO TO (100,200),NCFT
200  WRITE(6,2)X,DMEAN,F
      FORMAT(10X,'THE OPTIMUM HARD SPHERE DIAMETER WAS FOUND TO BE',
     * F12.5,3X,'THIS YIELDS AN AVERAGE VIRIAL COEFFICIENT OF',
     * F12.5,/,10X,'THE SUM SQUARED DEVIATION FROM THE MEAN =',
     * D15.5,/,/)
      GO TO 300
100  WRITE(6,29)X,DMEAN,F
29   FORMAT(10X,'VALUE OF X =',
     * F12.5,3X,'THIS YIELDS AN AVERAGE VIRIAL COEFFICIENT OF',
     * F12.5,/,10X,'THE SUM SQUARED DEVIATION FROM THE MEAN =',
     * D15.5,/,/)
C  WRITE HEADERS
300  WRITE(6,3)
3   FORMAT(10X,'VOLUME      RD DEN      ETA      DCFI      HSDCFI',
     * '  VIRIAL      CCALC      ERR IN C',/,/)
      S=C.000
      DO 10 I=1,NP
      RD=VC/V(I)
      CCAL=CHS(I)+DMEAN/V(I)
      PE=C(I)-CCAL
      S=S+CAES(PE)
10   WRITE(6,4)V(I),RD,E(I)*C(I)*CHS(I),DEL(I),CCAL,PE

```

```

//DLIST JOB '(1006,0643,5,9,,2001,2,N,48)', 'TELOTTE', CLASS=A, TYPRLN=COPY  JC
//ROUTE PRINT LOCAL
// EXEC FORTGC
//FURT.SYSIN ED *
C   PROGRAM TO CALCULATE P-V-T PROPERTIES OF ARGON
C   THIS PROGRAM USES THE GENERALIZED STROBRIDGE EQUATION
C   DEVELOPED BY THU,LEE AND STARLING FOR CALCULATIONS
C   FOR LIQUID ARGON
C   EQUATION OF STATE CALCULATIONS USING THE STROBRIDGE EQUATION
C   CALCULATIONS DONE WITH DIMENSIONLESS VARIABLES
C   THE LOCATION IN THE PROGRAM TO BE CHANGED FOR
C   USE OF DIFFERENT REDUCING PARAMETERS WILL BE INDICATED
C   CONSTANTS FOR THE DIFFERENT SUBSTANCES ARE TO BE ENTERED
C   IN A DATA STATEMENT
IMPLICIT REAL*8 (A-H,C-Z)
DIMENSION A(16)
DATA A/1.31024,-3.80636,-2.37238,-0.798872,0.198761,
* 1.47014,-0.7663672,0.19465,0.75429,0.7822,-0.94904,
* -15.6162,66.643,1E.527,9.04755,E.68282/
READ(5,1)NAME1,NAME2
1 FORMAT(2A4)
WRITE(6,2)NAME1,NAME2
2 FORMAT(10X,'EQUATION OF STATE CALCULATIONS FOR ',2A4,///)
READ(5,3)TMIN,TMAX,TINT
READ(5,3)RMIN,RMAX,FINT
3 FORMAT(3F10.4)
JCGINT=(TMAX-TMIN)/TINT+1
KCCJNT=(RMAX-RMIN)/RINT+1
DO 10 I=1,JCCJNT
T=TMIN+DFLOAT(I-1)*TINT
HERE IT HAS BEEN ASSUMED THAT THE MAX, MIN AND INTERVALS FOR
THE TEMPERATURE ITERATIONS HAS BEEN ENTERED IN DIMENSIONLESS
VARIABLES
CHANGE THE NEXT STATEMENT TO CHANGE THE FORM OF DIMENSIONLESS
TEMPERATURE. WE HAVE USED HERE INPUT AS T/TC AND THE
CALCULATIONS WILL BE DONE WITH K*T/EPISILON
THE RELATIONSHIP IS EPISILON/K=TC/1.2593
TS=1.2593047
4 WRITE(6,4)T,TS
FORMAT(10X,'REDUCED TEMPERATURE=',F9.4,5X,'TSTAR=',F9.4,///
* 10X,'REDUCED DENSITY',5X,'RHO STAR',10X,'Z ',EX,
* ' 1-C ',///)
C NOW DEFINE TEMPERATURE DEPENDENT FUNCTIONS REQUIRED
T1=1.000/TS
F1=A(1)+T1*(A(2)+T1*(A(3)+T1*(A(4)+A(5)*T1*T1)))
F2=A(6)+A(7)*T1
F3=A(E)
F4=T1*T1*T1*(A(9)+T1*(A(10)+A(11)*T1))

```

```

F5=TI*TI*TI*(A(12)+TI*(A(13)+A(14)*TI))
F6=A(15)*TI
CC 11 J=1,KCOUNT
R=RMIN+DFLCAT(J-1)*FINT
RS=0.21890C*R
C THE LAST STATEMENT SHOULD BE CHANGED TO USE DIFFERENT
C DENSITY VARIABLES. THE INPUT VALUES WERE R=RHC/RHOC
C THE PROGRAM USES RS=RHO*SIGMA**3 WITH THE CORRELATION
C SIGMA**3=0.3189/RHCC
C WILL NOW DEFINE DENSITY DEPENDENT FUNCTIONS
R2=RS*RS
R3=RS*RS*RS
R4=RS*RS*RS*RS
R5=RS*RS*RS*RS*RS
D1=-A(16)*R2
E1=DEXP(C1)
C NO CALCULATE THE Z AND DERIVATIVE OF THE Z
C WITH RESPECT TO THE DENSITY
F=F1+0.00+F1*RS+F2*R2+F3*R3+F4*R2*E1+F5*R4*E1+F6*RS
DF=FI+2.0DC*F2*RS+3.0D0*F3*R2+F4*E1*(2.0D0*RS
* -2.0C0*A(16)*R2)+F5*E1*(4.0D0*R2-2.0DC*A(16)*RS)
* +3.0C0*F6*RS
DMC=RS*DF+F
11 #WRITE(6.5)F,RS,F,DMC
5 FORMAT(13X,F9.4,6X,F9.4,10X,F9.4,12X,F9.4)
10 #WRITE(6,6)
5 FFORMAT(1H0)
11 STOP
END

```

----- JES2 JOB STATISTICS -----

26 AUG 61 JOB EXECUTION DATE

78 CARDS READ

0 SYSOUT PRINT RECORDS

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NERDC -- SYSTEM SUPPORT UTILITIES --

```

C PURPOSE: TO GENERATE P-V-T PROPERTIES OF LIQUID METHANE
C THIS PROGRAM USES THE EQUATION OF STATE OF MOLLERUP
C IMPLICIT REAL*8 (A-H,O-Z)
C GENERIC
COMMON A1,A2,A3,A4,B1,B2,B3,B4,C1,C2,C3,C4,C5,C6,D1,D2,D3,D4,D5
COMMON/DONE/AG,AL,BB,BE,DE,GK, TTRP,PTRP,DTRP, TCRT,PCRT,DCRT
COMMON/THRE/DPDT,D2PDT2,DLPDLR,DTSDR,DTHDR,DPS IDR, XB1,XB2,XD1,XD2
COMMON/FIVE/ P,T,DEN,DPDD, E,M,S, CV,CP,W, WK
COMMON/EIGHT/ COLDAT
COMMON/FOLF/FRT,DFDX,DFDR1
DIMENSION PP(16),VV(16),DMC(16)
CALL METHAN
100 READ(5,1,END=55)T
1 FORMAT(F10.0)
2 WRITE(6,2)
2 FORMAT(1H1,10X,'METHANE PROPERTIES FROM MOLLERUP',//)
3 TR=T/TCRT
3 WRITE(6,3)T,TR
3 FORMAT(10X,'TEMPERATURE =',F10.3,//
5 '          REDUCED TEMPERATURE =',F10.4,//)
5 WRITE(6,4)
5 FORMAT(10X,'           PRESSURE           VOLUME           1-C*',//)
5 BASE=15.225DC
5 DINC=1.015CC
5 DO 10 I=1,16
5 VV(I)=BASE+DFLOAT(I-1)*DINC
5 PP(I)=DPDRF(T,VV(I))
5 DMC(I)=DLPDLR*PP(I)/VV(I)/T/GK
5 VV(I)=1.0D-3/VV(I)
5 PP(I)=PP(I)/1.01325D0
10 WRITE(6,5)PP(I),VV(I),DMC(I)
5 FORMAT(10X,3F15.4)
5 WRITE(7,5)T
5 WRITE(7,6)PP,VV,DMC
5 WRITE(7,6)T
6 FORMAT(3F10.3)
6 GO TO 100
99 STEP
END
SUBROUTINE METHAN
C NOTE THAT PRESSURES ARE IN BARS. 1 ATM = 1.01325 BAR.
C ONE BAR-LITER = 100 JOULES.
C*
IMPLICIT REAL*8 (A-H,O-Z)

```

```
GENERIC
COMMON A1,A2,A3,A4,B1,B2,B3,B4,C1,C2,C3,C4,C5,C6,D1,D2,D3,D4,D5
COMMON/ONE/AG,AL,BB,BE,DE,GK, TTRP,PTRP,DTRP, TCRT,PCRT,DCRT
COMMON/THERE/DPT,D2DPT2,DLPDLR,DTSDR,DTHDR,DPSIDR, XB1,XB2,XD1,XD2
COMMON/FIVE/ F,T,DEN,DPOD, E,H,S, CV,CF,W, WK
COMMON/EIGHT/ DDLOT
C CONSTANTS FROM MARSFCAS 9/3/71.
      WRITE(6,SS)
      SS FORMAT(30H *** CH4 *** JANUARY 20 1976 ) )
      TTRP=90.68
      PTRP=0.117435675
      CTRP=29.1472
C      PCRT = 45.556467    BAR
      TCRT=190.53
      PCRT=PSATF(TCRT)
      DCRT=10.15
      AG=.5
      AL=.3
      BB=.8
      BE=.0
      DE=.2
      GK = 0.0831434
      CJ = 100
      WK = 101325/16.043
      A1=-4.15452847
      A2=-4.77390186
      A3=3.1999044
      A4=4.25737412
```

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```

31=1.74744E56
32=2.57679E69
E3=0.46538980
C1=5.10335531
C2=-12.42022748
C3=6.36124273
D1=1.EE383919
D2=-3.54713477
D3=1.87406E15
RETURN
ENC
FUNCTION PSATF(T)
C METHANE VAPCR PRESSURE VIA PRYDZ/GCCDWIN DATA, NOV., 1970.
C NOTE, PRESSURE IN BARS, 1.01325 BAR/ATM.
IMPLICIT REAL*8 (A-H,O-Z)
COMMON/THRE/DPDT,D2PDT2,DLPDLR,DTSDR,DTHDR,DPSIDR, XB1,XB2,XC1,XD2
GENERIC
DATA PTRP / 0.117435675/, TTRP/90.68/, TCRT/190.53/, E/1.E/
DATA A/4.7732553/, B/1.7665879/, C/-0.5702812/, D/1.3311873/
1 XK=1-TTRP/TCRT
X=(1-TTRP/T)/XK
C=1-X
IF(C) 2,3,4
2 PSATF = 0
DFCT = 0
RETURN
3 W=0
W1=0
GO TO 5
4 * = 0**5
W1 = -F*W/C
5 DX=T=TTRP/XK/T**2
2=X**4
Z1 = W + X*W1
6 FZ = A*X + B*X**2 + C*X**3 + D*Z
7 F1 = A + 2*C*X + 3*C*X**2 + D*Z1
8 PSATF=PTRP*EXP(FZ)
DPCT=PSATF*F1*DXDT
RETURN
END
FUNCTION DENL IQ(T)
C METHANE SATD.LIQUID DENSITIES VIA GCCDWIN.
C THIS FUNCTION REFITTED VIA ,DENSATLQ, 4/29/71.
IMPLICIT REAL*8 (A-H,O-Z)

```

```

GENERIC
CCPMCN/EIGHT/ DCDDT
DATA TCRT/190.53/,DCRT/10.15/
DATA A/0.E39403/, B/1.E96635/, C/-0.01E387/, E/0.88/
L X = T/TCRT
    Z = 1 - X
    IF(Z.LT..01) GO TO 7
2 F = -E*X**2/Z
    XP = EXP (F)
3 DFDX = -E*(2 + X/Z)*X/Z
    C = Z**0.36
4 G = A*Z + E*Q + C*XP
    DENLIC = DCRT*(1+G)
5 G1 = C*XP*DFDX - A - 0.36*B*Q/Z
6 DCDDT = DCRT*G1/TCRT
    RETURN
7 IF(Z.LT.1.E-09) Z=1.E-09
    C=Z**0.36
    G=A*Z + B*C
    DENLIC = DCRT*(1+G)
    G1 = -A - .36*B*Q/Z
    DCDDT = DCRT*G1/TCRT
    RETURN
    END
FUNCTION TSATF(DEN)
C TSAT(DEN) FORMULA. METHANE, CONSTRAINED TO TRIPLE POINT. IPTS-68.
C YIELDS ALSO THE FIRST DERIVATIVE RSP. TO RHC>DEN/DTRP.
C EQN.. (TCRT/T-1)/AZ = F(R) = U(S)*(1 + AI*LCG(R) + (R-1)*W(R)).

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C WHERE, U(S) = ((S-1)/(ST-1))**(8/3), AZ = (TCRT/TTRP-1), AND -
C W(R) = A2 + A3*R + ... + A8*R6.
C IMPLICIT REAL*8 (A-H,O-Z)
C GENERIC
C COMMON/DEN/AG,AL,BB,BE,DE,GK, TTRP,PTRP,DTRP, TCRT,PCRT,DCRT
C COMMON/THRE/DPDT,D2PDOT2,DLPDLR,DTSDR,DTHDR,DPSIDR, XB1,XB2,XD1,XD2
C DIMENSION A(8)
C DATA A / -0.142445, 2.4794529, -6.7596384, 41.05600105,
C      1-133.4449230, 223.4955973, -181.8267154, 58.8359684/
1 AZ = TCRT/TTRP - 1
  CSDR = DTRP/DCRT
  SK = DSDR - 1
2 R=DEN/DTRP
  S=CEN/CCRT
  IF((S-1)/SK.LT.0.) Q=-AES((S-1)/SK)**.333333
  IF((S-1)/SK.GE.0.) Q=((S-1)/SK)**.333333
  IF(Q) 3,S,3
3 U = Q**2
  U1 = 8*CSDR*Q**5/SK/3
4 V = R-1
  d=C
  w1=0
  CO 6 K=2,2
5 * = W + A(K)*R***(K-2)
  w1 = w1 + (K-2)*A(K)*R***(K-3)
6 CCNTINUE
  G=DLLOG(R)
  F = U*(1 + A(1)*G + V**W)
7 F1 = U1 + A(1)*(U/R + U1*G) + U*V*w1 + U**W + U1*V**W
8 TSATF=TCRT/(1+AZ*F)
  CTSDF=(AZ/TCRT)*F1*TSATF**2
  RETURN
9 TSATF = TCRT
  CTSDF = 0
  RETURN
END
FUNCTION TFETAF(CEN)
IF S .NE. 1, L = AG*(S-1)**3.  IF S .EQ. 1, U = -AL*(S-1)**3.
YIELDS ALSO THE FIRST DERIVATIVE RSP. TO RHO>DEN/DTRP.
IMPLICIT REAL*8 (A-H,O-Z)
GENERIC
COMMON/DEN/AG,AL,BB,BE,DE,GK, TTRP,PTRP,DTRP, TCRT,PCRT,DCRT
COMMON/THRE/DPDT,D2PDOT2,DLPDLR,DTSDR,DTHDR,DPSIDR, XB1,XB2,XD1,XD2
1 S=DEN/DCRT

```

```
DSDR = DTDF/DCRT
IF(S) 9*5+2
2 G=S-1
Q2=Q*2
Q3=Q**3
IF(Q) 3*8+4
3 U = AG*Q3
U1 = 3*AG*G2*DSDR
GU TC 5
4 J = -AL*Q3
U1 = -3*AL*G2*DSDR
5 IF(U.LT.-5C.) L=-50.
XP = EXP(U)
TS = TSATF(CEN)
THETAF = 1E+XP
7 CTHDR = TS*U1*XP + DTSDR*XP
RETURN
8 THETAF = TCRT
CTHOR = 0
RETURN
9 THETAF = 0
DTHOR=1.E 05
RETURN
END
FUNCTION PHI(T)
C XB = PHI = X*(1-EXP(-U)), U = BE + BE/X,
C YIELDS ALSC DPHI/DR, DPHI/DX, AND D2PHI/DX2.
C IMPLICIT REAL*8 (A-H,O-Z)
```

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```

GENERIC
COMMON/DONE/AG,AL,BB,BE,DE,GK, TTRP,PTRP,DTRP, TCRT,PCRT,DCRT
COMMON/TRE/DPDT,D2PDT2,DLPDLR,DTSDR,DTHDR,DPSIDR, XB1,XB2,XD1,XD2
1 X=T/TCRT
U=BB*BE/X
U1=-BE/X**2
U2=-2*U1/X
2 XP=EXP (-U)
Z=1-XP
Z1=U1*XP
Z2=(U2-U1**2)*XP
3 PHIF = X*Z
XB1 = X*Z1 + Z
XB2 = X*Z2 + 2*Z1
9 RETURN
END
FUNCTION PSIF(T,DEN)
C  X0 = PSI = (1-W*LOG(1+1/W))/X,   W = (T-TH)/(DE*TCRT).
C  YIELDS ALSO XD1 > DPSI/DX, XD2 > D2PSI/DX2, AND DPSI/DR.
C  IMPLICIT REAL*8 (A-F,0-Z)
GENERIC
COMMON/DONE/AG,AL,BB,BE,DE,GK, TTRP,PTRP,DTRP, TCRT,PCRT,DCRT
COMMON/TRE/DPDT,D2PDT2,DLPDLR,DTSDR,DTHDR,DPSIDR, XB1,XB2,XD1,XD2
1 TH = THETAF(DEN)
W = (T-TH)/DE/TCRT
IF(W) 2,2,3
2 PSIF=1
XD1=0
XD2=0
DPSIDR=0
RETURN
3 X=T/TCRT
DCR=DTHDR/DE/TCRT
DCX=1/DE
4 U=1/X
DCUX=-U/X
D2JDX2=-2*DCUX/X
5 G=DLLOG(1.0DC+1.0DD/W)
WS = 1+W
V = 1-W*G
6 DVDW = 1/WS-G
C2VDW2 = 1/W/WS**2
PSIF = U*V
7 DPSIDR = U*DWDW*DWDW

```

```

XD1 = U*DUDX*DUDX + V*DUDX
8 XD2 = U*D2UDX**2*DUDX**2 + 2*DUDX*DUDX*DUDX + V*D2UDX2
9 RETURN
END
FUNCTION DPDRF(T,DEN)
C NOTE. DPDRF = PRESSURE, BAR.
C REDUCED DERIVATIVE. DLDPDLR > R*(DP/DR)/P IS IN COMMON.
C (2-1)*X/R = F(T,R) YIELDS (DP/DR)/DTRP/GK/T = 1+(R2*F1+2*R*F)/X.
C IMPLICIT REAL*8 (A-H,O-Z)
C GENERIC
COMMON A1,A2,A3,A4,B1,B2,B3,B4,C1,C2,C3,C4,C5,C6,D1,D2,D3,D4,D5
COMMON/DNE/AG,AL,BB,BE,DE,GK, TTRF,PTRP,DTRP, TCRT,PCRT,DCRT
COMMON/THRE/DPDT,D2PD2,DLDPDLR,DTSDR,DTHDR,DPSIDR, XB1,XB2,XD1,XD2
COMMON/FCUF/FFT,DFDX,DFDR1
1 X=T/TCRT
S=DEN/DCRT
DSR = DTRF/DCRT
2 R=DEN/DTRP
R2=R**2
R3=R**3
3 XB = PHIF(T)
XC = 1/X
4 XD = PSIF(T,DEN)
XDD = CPSICR
6 A = A1 + A2*R + A3*R2 + A4*R3
AC = A2 + 2*A3*R + 3*A4*R2
7 B = B1 + E2*R + E3*R2
BD = B2 + 2*B3*R

```

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```
 8 C = C1*R + C2*R2 + C3*R3
 9 CD = C1 + 2*C2*R + 3*C3*R2
10 U = S-1
11 LI = DSQR
11 V = D1 + D2*R + D3*R2
12 VI = D2 + 2*D3*R
14 D = U*V
15 DC = U*VI + U1*V
16 F = A + E*X E + C*X C + D*X D
16 DFDR = AD + BD*X B + CD*X C + D*X DC + DD*X D
17 G = 1 + (R2*DFDR + 2*R*F)/X
    G=1+F*R/X
    DLDPOLR = G/Q
20 DFCRF = DEN*GK*T*Q
DFDR1=DFDR
      RETURN
      END
```

END OF FILE ON SYSIN.

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```

C REGRESSION PROGRAM TO FIND T*,V*, AND K(I,J) USING PURE
C COMPONENT DATA
C IMPLICIT REAL*8 (A-H,O-Z)
C DIMENSION DIN1(3),DIN2(8),DIN3(8),NC(20),T(20,110),P(20,110),
C * RO(20,110),RKT(20,110),ANU(20,5),BNU(5),TS(5),VS(5),AK(5,5),
C * NCOR(6,5),F(2000),X(15),W(I2000),CT(20),CV(20),RES1(20,110),
C * RES2(20,110),NAME(25),NTITLE(20,25)
C LIMITATIONS--- 20 COMPONENTS
C           5 GROUPS
C           110 DATA POINTS PER COMPONENT
C UNITS----- PRESSURE IN ATMS OR EARS (OPTION 18)
C           VOLUMES IN CC/GMOL
C           TEMPERATURES IN KELVIN
C NOTES----- NAME IS FORTY CHARACTERS
C           USE ONE BLANK CARD AT THE END OF A COMPONENT DATA SET
C           USE ANOTHER BLANK CARD AT THE END OF ALL THE DATA
C
C SET UP COMMON BLOCKS
COMMON /DATA/ T,P,RO,RKT,ANU
COMMON /PARAM/ TS,VS,AK
COMMON /DECIPH/ NCOR,NG,ND,NNM
COMMON /RESULT/ RES1,RES2
C NOPT DETERMINES IF A REGRESSION OR A CALCULATION IS TO BE PERFORMED
C IF NOPT IS 0 THEN THE REGRESSION PROCEEDS ANY OTHER VALUE
C IF NOPT CAUSES ONLY A CALCULATION TO BE PERFORMED
READ(5,47)NOPT
47 FORMAT(1I1)
C FIRST INPUT IS THE NUMBER OF DIFFERENT GROUPS
999 READ(5,1,END=999)NG
1 FORMAT(1I2)
C INITIALIZE COUNTER FOR NUMBER OF MOLECULES
NNM = 0
C ENTER DATA FOR FIRST COMPONENT
2000 READ(5,2) NAME,TC,VC
2 FORMAT(25A2,2F10.0)
C CHECK TO SEE IF ALL DATA HAS BEEN INPUT
IF(TC.LT.1.000) GO TO 7777
C NU IS THE STOICHIOMETRIC VECTOR FOR THE COMPONENT
READ(5,25)(ENU(I),I=1,NG)
25 FORMAT(5F10.0)
C UPDATE COMPONENT COUNTER
NNM = NNM + 1
C SET COUNTER FOR NUMBER OF DATA POINTS FOR EACH MOLECULE
ND(NNM) = 0

```

```
C      BEGIN PACKING INPUT DATA
DC 50 I=1,10
50  NTITLE(NNM,I) = NAME(I)
CT(NNM) = TC
CV(NNM) = VC
DO 75 I=1,NG
75  ANU(NNM,I) = ENU(I)
C      ENTER OPTION FOR PRESSURE UNITS
READ(5,3) IB
3   FORMAT(II)
1000 READ(5,4) TEMP
4   FORMAT(F10.0)
C      CHECK TO SEE IF END OF A COMPONENT DATA SET
IF(TEMP.LT.1.000) GO TO 2000
READ(5,5) DIN1,DIN2,DIN3
5   FORMAT(BF10.0)
C      CHECK TO SEE IF TOO CLOSE TO CRITICAL TEMPERATURE
CHECK = DAES(TEMP/TC - 1.000)
IF(CHECK.LT.0.0500) GO TO 1000
C      CHECK ON PRESSURE UNITS AND CONVERT BARS TO ATMS
IF(IB.EQ.0) GC TC 3000
DO 100 I=1,E
100 DIN1(I) = DIN1(I)/1.01325
C      CHECK FOR ZERO DATA POINTS, COUNT AND PACK
3000 DC 200 I=1,8
IF(DIN1(I).LT.1.000.OR.DIN2(I).LT.1.000) GO TO 200
IF(VC/DIN2(I).LT.1.300) GO TC 200
ND(NNM) = ND(NNM) + 1
```

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```

NDUM = ND(NNM)
T(NNM,NDUM) = TEMP
P(NNM,NDUM) = DIN1(I)
R0(NNM,NDUM) = 1.0D0/DIN2(I)
200 CONTINUE
C RETURN FOR ANOTHER ISOTHERM
GO TO 1000
C AFTER ALL DATA IS IN ENTER KNOWN PARAMETERS AND FLAGS FOR
C THOSE TO BE FOUND BY THE ROUTINE
C ENTER A NEGATIVE VALUE OF T* OR V* IF IT IS TO BE FOUND BY THE
C PROGRAM. THE INITIAL GUESS WILL BE NEGATIVE THE INPUT VALUE
C ENTER K>1 IF IT IS TO BE FOUND
C FIND TOTAL NUMBER OF DATA POINTS
7777 NSUM = 0
      DO 300 I=1,NNM
300  NSUM = NSUM + ND(I)
C ENTER T* AND V*
      READ(5,6)(TS(I),I=1,NG)
      READ(5,6)(VS(I),I=1,NG)
      FORMAT(SF10.0)
C FIND NUMBER OF UNKNOWNNS AND SET UP CORRELATION MATRIX TO BE
C ABLE TO RETRIEVE THEM LATER
C INITIALIZE COUNTER FOR NUMBER OF REGRESSION PARAMETERS
1987 NP=0
      NGP = NG + 1
      DO 400 I=1,NGP
      DO 400 J=1,NG
400  NCOR(I,J) = 0
      DO 500 I=1,NG
      IF(TS(I).GT.1.0D0) GO TO 5000
      NP = NP + 1
      NCOR(I,I) = NP
C SET INITIAL GUESSES AS -1.0D0*TS(I)
      X(NP) = -1.0D0*TS(I)
500  IF(VS(I).GT.1.0D0) GO TO 500
      NP = NP + 1
      NCOR(2,I) = NP
      X(NP) = -1.0D0*VS(I)
500  CONTINUE
C NOW WILL READ K'S AND FIND UNKNOWNNS ONES AND ENTER INITIAL GUESSES
C NOTICE THAT ONLY THE FIRST NG-1 ROWS OF AK MUST BE ENTERED
C REMEMBER TO ENTER K>1 IF UNKNOWN
      AK(1,1) = 0.000
      IF(NG.EQ.1) GO TO 3333

```

```
      NGM = NG - 1
      DO 600 I=1,NGM
500  READ(5,7)(AK(I,J),J=1,NG)
7    FORMAT(1SF1C.0)
      DO 650 I=1,NG
650  AK(NG,I) = 0.000
      DO 700 I=1,NGM
      IP=I+1
      DO 700 J=IP,NG
      IF(AK(I,J).LT.1.0D-10) GO TO 700
      NF = NP+1
      X(NP) = 0.000
      IP2 = I+2
      NCCR(IP2,J) = NP
700  CONTINUE
C     CHECK TO SEE IF IN REGRESSION OR CALCULATION MODE
3333 IF(NOPT.NE.0) GO TO 3335
C     BEGIN REGRESSION
      CALL VA05AC(NSUM,NP,F,X,1.0D-1,1.002,1.0D-3,99,10,W)
C     AFTER REGRESSION COMPLETE CALCULATE FUNCTIONS ONE MORE TIME FOR OUTP
3335 CALL CALFUN(NSUM,NP,F,X)
C     CALCULATE AVERAGE ERROR FOR ALL DATA POINTS REALIZING THAT THE
C     FIRST DATA POINT ON EACH ISOTHERM HAS ZERO ERROR AND SHOULD NOT BE
C     COUNTED
      NZ = 0
      SUMERR = 0.000
      DO 300 I=1,NSUM
      SUMERR = SUMERR + DABS(F(I))
```

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      IF(F(1).NE.0.000) GO TO 800
      NZ = NZ+1
300  CONTINUE
      AVGABS = SUMERR/(NSUM-NZ)
C      BEGIN GENERAL CPUTPUT
      WRITE(6,11)
11     FFORMAT(1H1,20X,'SUMMARY OF RESULTS '///)
      WRITE(6,12)
12     FFORMAT(20X,'CHARACTERISTIC PARAMETERS'///
      * 20X,'GROUP NUMBER',10X,' TSTAR ',10X,' VSTAR '///
      * 20X,'CALCULATED FOR ',13,' DATA POINTS '///)
      WRITE(6,13)(I,TS(I),VS(I),I=1,NG)
13     FFORMAT(25X,I2,16X,F7.2,10X,F7.2)
      WRITE(6,14)
14     FFORMAT(//,20X,' K MATRIX '///)
      DO 1200 I=1,NG
1200  WRITE(6,15)(AK(I,J),J=1,NG)
15     FORMAT(20X,5(F10.4,5X),///)
      NNN = NSUM - NZ
      WRITE(6,16)AVGABS,NNN
16     FFORMAT(20X,'THE AVERAGE ABSOLUTE ERROR WAS ',F15.4,/
      * 20X,'CALCULATED FOR ',13,' DATA POINTS '///)
C      BEGIN INDIVIDUAL COMPONENT PRINTOUT
      NF=0
      DO 900 II=1,NNN
      WRITE(6,17)
17     FORMAT(1H1)
      WRITE(6,18)(NTITLE(II,I),I=1,25)
18     FFORMAT(10X,25A2,///)
      WRITE(6,19)CT(II),CV(II)
19     FORMAT(10X,'CRITICAL CONSTANTS'///
      * 10X,'TEMPERATURE--',F7.2/
      * 10X,'VOLLMC-----',F7.2//)
      WRITE(6,21)(ANU(II,I),I=1,NG)
21     FFORMAT(10X,'STOICHIOMETRIC VECTOR'///
      * 15X,5F7.4//)
      WRITE(6,22)
22     FFORMAT(10X,'TEMP',4X,'PRESSURE',2X,'VOLUME',2X,'DENSITY',2X,
      * 'DEL_PX',4X,'DEL_Pc',4X,'ERROR',4X,'%ERROR',///)
      NDLM=ND(II)
      SUMI=C.0D0
      NCOUNT = 0
      DO 1300 LBJ=1,NDLM
      VF=VF+1
      VCL = 1.0D0/RD(II,LEJ)

```

```

      NNCJ4=NF
13500  ERA = RES2(II,LBJ)-RES1(II,LBJ)
      *RITE(6,23)T(II,LBJ),P(II,LBJ),VCL,RO(II,LBJ),RES1(II,LBJ),
      * RES2(II,LBJ),ERR,F(NNDUM)
23   FORMAT(9X,F7.2,2X,F7.2,1X,F7.3,2X,F7.4,1X,F8.3,1X,F8.3,1X,F8.3,
      * 1X,F9.3)
      SUMI=SUMI+CAES(F(NNDUM))
      IFF(NNDUM).NE.0.0D0) NCOUNT = NCOUNT+1
1300  CONTINUE
      AERRI = SUMI/NCOUNT
      WRITE(6,24)AERRI
24   FURAT(///,20X,'AVERAGE ABSOLUTE ERROR = ',F10.4,///)
900   CONTINUE
      GO TO 999
9999 STOP
      END
      SUBROUTINE CALFUN(NSUM,NP,F,X)
C THIS SUBROUTINE IS USED BY VA05AD FOR THE REGRESSION
C ALL UNITS AND RESTRICTIONS ARE THE SAME AS FOR THE MAIN ROUTINE
      IMPLICIT REAL*8 (A-F,O-Z)
      DIMENSION NC(20),T(20,110),P(20,110),RC(20,110),RKT(20,110),
      * ANU(20,5),TS(S),VS(S),AK(S,S),NCCR(6,5),F(2000),X(15),
      * RES1(20,110),RES2(20,110),ANUI(5),TI(110),PI(110),RO(110)
C SET UP COMMON BLOCKS FOR COMMUNICATION
      COMMON /DATA/ T,P,RO,RKT,ANU
      COMMON /PARAM/ TS,VS,AK
      COMMON /DECIPH/ NCCR,NG,ND,NM
      COMMON /RESULT/ RES1,RES2

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COMMON /SAVE/ III
C FIRST SORT X VECTOR TO RECOVER PARAMETERS
1983  JC 100 J=1,NG
      IF(NCOR(1,J).NE.0) TS(J)=X(NCOR(1,J))
      IF(NCOR(2,J).NE.0) VS(J)=X(NCOR(2,J))
      IF(NG.EQ.1) GO TO 100
      NGP = NG + 1
      CC 110 I=3,NGP
      IM=I-2
      IF(ICOR(I,J).NE.0) AK(IM,J)=X(NCOR(I,J))/100.0D0
110  CCNTINUE
100  CCNTINUE
      IF(NG.EQ.1) GO TO 250
      NGM = NG-1
      DC 200 I=1,NGM
      IP = I+1
      DO 200 J=IP,NG
      AK(J,I) = AK(I,J)
200  CONTINUE TC RECOVER PARAMETERS WHILE CALCULATING FUNCTIONS
C GUTER LOOP PERFORMS CALCULATIONS FOR ALL MOLECULES
250  NF = 0
      DC 300 II=1,NMM
      NDUM=ND(II)
C SORT STOICHIOMETRIC MATRIX
      JC 400 JJ=1,NG
400  ANL(JJ)=ANL(II,JJ)
C SORT T,P,R#D
      JC 500 KK=1,NCUM
      TI(KK) = T(II,KK)
      PI(KK) = P(II,KK)
      RC1(KK) = FC(II,KK)
500  TOLD=C.0D0
      DC 300 L=1,NDUM
      NF=NF+1
      IF(DABS(TI(L)-TOLD).LT.0.01D0) GO TO 6000
      III=0
      TOLD=TI(L)
      TR=TI(L)
      PR=PI(L)
      RR=RC1(L)
      CALL GP(NG,RR,ANUI,AK,TS,VS,TR,PRC)
6000  III=1

```

```

TM=TI(L)
PM=PI(L)
RM=RGI(L)
CALL GP(NG,RM,ANU,AK,TS,VS,TH,PMC)
RES1(II,L) = PM-PR
RES2(II,L) = PMC-PRC
NNUM=NF
5750 IF(RES1(II,L).GT.+1.0D0) GO TO 6760
F(NNUM) = 0.0D0
GO TO 300
6760 F(NNUM) = (RES2(II,L)/RES1(II,L) - 1.0D0)*100.0D0
300 CONTINUE
RETURN
END
SUBROUTINE GR(NG,RHC,ANU,AK,TS,VS,T,P)
C PURPOSE: TO CALCULATE THE PRESSURE OF A PURE COMPCNENT
C           USING THE GROUP CNTRIBUTION EQUATION OF STATE
C VARIABLES: NG--THE NUMBER OF DIFFERENT TYPES OF GROUPS
C             RHC--THE DENSITY IN GMOLE/CC
C             ANU--THE VECTOR OF STOICHIOMETRIC COEFFICIENTS
C             AK--THE MATRIX OF BINARY INTERACTIONS CONSTANTS
C             TS--THE VECTOR OF CHARACTERISTIC TEMPERATURES IN K
C             VS--THE VECTOR OF CHARACTERISTIC VOLUMES IN CC/GMOLE
C             T--THE TEMPERATURE IN K
C             P--THE PRESSURE CALCULATED IN ATM
C SUBROUTINES REQUIRED: SIGMA
C                         VIRIAL
C                         BPHS

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C
C      IMPLICIT REAL*8 (A-H,C-Z)
C      DIMENSION RG(10),ANU(5),AK(5,5),TS(5),VS(5),B(5,5),SIG(5),
*     SIGM(10,10)
C      RG IS THE VECTOR OF GROUP DENSITIES
C      B IS THE MATRIX OF GENERALIZED VIRIAL COEFFICIENTS
C      SIG IS THE VECTOR OF HARD SPHERE DIAMETERS
C      SIGM IS THE MATRIX OF HARD SPHERE DIAMETERS
C      COMMON /SAVE/ III
C      III IS USED TO DETERMINE IF THE TEMPERATURE HAS CHANGED
C      IF III IS C ALL CALCULATIONS ARE PERFORMED
C      IF III IS NONZERO ONLY THE HARD SPHERE PRESSURE IS CALCULATED
C      III SHOULD BE 0 FOR THE FIRST CALL ON AN ISOTHERM
C      CONSTANTS ARE DEFINED
C      PI=3.1415926525D0
C      R=82.056D0
C      CALCULATE THE TOTAL NUMBER OF GROUPS AND THE GROUP DENSITIES
C      TNG=G.0D0
C      DO 10 I=1,NG
C      TNG = TNG + ANU(I)
10    RG(I) = ANU(I)*RHO
C      CHECK TO SEE IF TEMPERATURE HAS CHANGED
C      IF(III.GT.0) GO TO 100
C      CALCULATE HARD SPHERE DIAMETERS AND VIRIAL COEFFICIENTS
C      CALL SIGMA(NG,T,TS,VS,SIG)
C      CALL VIRIAL(NG,T,TS,VS,AK,B)
C      CALCULATE PERTURBATION TERM
C      VC=0.0D0
C      DO 30 I=1,NG
C      DO 30 J=1,NG
30    VC = VC + ANU(I)*ANU(J)*B(I,J)
C      CALCULATE THE HARD SPHERE CONTRIBUTION
100   CALL BPHS(NG,RG,SIG,HSBP)
C      ADD ALL CONTRIBUTIONS TOGETHER
C      BP=HSBP-RHO*RHO*VC/2.0D0+RHO*(1.0D0-TNG)
C      CALCULATE THE ACTUAL PRESSURE
C      P=BP*R*T
C      SET III>0 FOR NEXT PASS THROUGH THE ROUTINE
III=1
C      RETURN
ENC
      SUBROUTINE SIGMA(NG,T,TS,VS,SIG)
C      THIS SUBROUTINE WILL CALCULATE THE VECTOR OF HARD SPHERE
C      DIAMETERS USED IN THE HARD SPHERE PRESSURE CALCULATION

```

C THE FUNCTIONAL FORM USED FOR THE TEMPERATURE DEPENDENCE
C IS A MODIFICATION OF THAT PROPOSED BY BIENKOWSKI AND
C CHAD FOR THE INERT GASES
C VARIABLE LIST:
C NG - THE NUMBER OF GROUPS
C T - THE TEMPERATURE IN KELVIN
C TS - THE VECTOR OF CHARACTERISTIC TEMPERATURES
C FOR THE GROUPS CONSIDERED IN KELVIN
C VS - THE VECTOR OF CHARACTERISTIC VOLUMES FOR
C THE GROUPS IN CC/GMOLE
C SIG - THE VECTOR OF HARD SPHERE DIAMETERS THE
C UNITS ARE SUCH THAT RHO*SIG**3 IS
C DIMENSIONLESS IF RHO IS IN GMOLE/CC
C THERE ARE NO OTHER SUBROUTINES REQUIRED
C LIMITED TO 5 GROUPS --- THIS CAN BE CHANGED BY ALTERING
C THE DIMENSION STATEMENT
C IMPLICIT REAL*8 (A-H,O-Z)
C ALL CALCULATIONS IN DOUBLE PRECISION
DIMENSION TS(5),VS(5),SIG(5)
DIMENSION XC(6)
DATA XC/0.1383200,0.26446D-1,0.80057D-1,-0.89999D-1,0.390E5D-1,
* -0.60984D-2/
C DEFINE CONSTANTS REQUIRED
PI = 3.141592653500
T3 = 1.000/3.000
C ALL CALCULATIONS IN ONE LOOP
DO 10 I=1,NG
TR = T/TS(I)

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20      TRI=1.0D0/TR
F=XC(1)+TR*(XC(2)+TR*(XC(3)+TR*(XC(4)+TR*(XC(5)+TR*XC(6)))))

10      SIG(I)=(6.0D0*F*VS(I)/PI)**T3
RETURN
END
SUBROUTINE VIRIAL(NG,T,TS,VS,AK,B)
C PURPOSE: TO CALCULATE THE MATRIX OF VIRIAL COEFFICIENTS
C VARIABLES: NG-NUMBER OF DIFFERENT TYPES OF GROUPS
C             T-THE TEMPERATURE IN K
C             TS-THE VECTOR OF CHARACTERISTIC TEMPERATURES
C             VS-THE VECTOR OF CHARACTERISTIC VOLUMES IN CC/GMOLE
C             AK-THE MATRIX OF BINARY CONSTANTS
C             B-THE MATRIX OF VIRIAL COEFFICIENTS IN CC/GMOLE
C
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION TS(5),VS(5),AK(5,5),B(5,5),TR(10,10),VR(10,10),
$ A(5)
C TR IS A MATRIX OF CHARACTERISTIC TEMPERATURES
C VR IS A MATRIX OF CHARACTERISTIC VOLUMES
C A IS A VECTOR OF CONSTANTS FOR THE VIRIAL COEFFICIENT CORRELATION
C DATA A/5.0E10,-2.321D1,5.0E27D1,-4.0E62D1,1.5618D1,-2.3173D0/
C DEFINE CNE CONSTANT NEEDED
T3=1.0D0/3.0D0
C ALL CALCULATIONS INSIDE ONE LOOP
DO 10 I=1,NG
DO 10 J=I,NG
IF(I-J) 1,2,1
1   TR(I,J)=DSQRT(TS(I)*TS(J))*(1.0D0-AK(I,J))
VR(I,J)=((VS(I)**T3+VS(J)**T3)**3)/B(0,0)
GO TO 3
2   TR(I,J)=TS(I)
VR(I,J)=VS(I)
3   TI=TR(I,J)/T
B(I,J)=(A(1)+TI*(A(2)+TI*(A(3)+TI*(A(4)+TI*(A(5)+TI*A(6)))))*
$ VR(I,J)
B(J,I)=B(I,J)
CONTINUE
RETURN
END
SUBROUTINE SPHS(NG,RG,SIG,FSPH)
C PURPOSE: TO CALCULATE THE PRESSURE OF A COLLECTION OF HARD
C SPHERES USING THE GENERALIZED HARD SPHERE EQUATION
C NOTE: THE OUTPUT IS ACTUALLY BETA*F IN GMOLE/CC
C VARIABLES: NG-THE NUMBER OF DIFFERENT TYPES OF GROUPS
C             RG-VECTOR OF GROUP DENSITIES IN GMOLE/CC

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```
C           SIG-THE VECTOR OF HARD SPHERE DIAMETERS
C           HSBP-BETA*P FOR THE HARD SPHERES IN GMOLE/CC
C
C           IMPLICIT REAL*8 (A-H,O-Z)
C           DIMENSION FG(10),SIG(5)
C           DATA AL/-4.2D0/
C           ENTER THE VALUE OF PI
C           PI=3.1415926525D0
C           ZERO REGISTERS FOR CALCULATION OF SUMMATIONS
C           Z0=0.0D0
C           Z1=0.0D0
C           Z2=0.0D0
C           Z3=0.0D0
C           CALCULATE SUMS
C           DO 10 I=1,NC
C           ADD=PI/6.0D0*FG(I)
C           ZC=Z0+ADD
C           Z1=Z1+ADD*SIG(I)
C           Z2=Z2+ADD*SIG(I)*SIG(I)
C 10      Z3=Z3+ADD*SIG(I)*SIG(I)*SIG(I)
C           DUM=1.0D0/(1.0D0-Z3)
C           P1=Z0*DUM
C           P2=1.0D0*Z1*Z2*DUM*DUM
C           P3=Z2*Z2*Z2*DUM*DUM*DUM*(3.0D0+AL*Z3)
C           HSBP=(6.0DC/PI)*(PI+P2+P3)
C           RETURN
C           END

END OF FILE ON SYSIN.
```

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C      PROGRAM TO CALCULATE REDUCING VOLUME CORRECTION FOR THE HARD
C      CONVEX BODY EQUATION OF STATE
C      VERSION CF 2MARCH 1980
C      INPUT VARIABLES ARE :
C      1. AL      SHAPE FACTOR OF INTEREST (R*S/3V)
C      2. B       LOWER LIMIT OF INTEGRATION FOR PACKING FRACTION
C      3. T       UPPER INTEGRATION LIMIT
C
C      SUBROUTINES AND FUNCTIONS REQUIRED
C      RQUADD,EVALFUNCTN,FV,GV,GALES
C      IMPLICIT REAL*8 (A-F,O-Z)
C      DIMENSION FCL(10),INA(3)
C      COMMON X,AL
C      EXTERNAL FUNCTN
1000 READ(5,1,END=900) AL
   1 FORMAT(D10.3)
   3=C2D0
   T=0.55D0
   X=0.9D0+0.144C0*AL
   ITEST=2
10 CALL RQUADC(ITEST,X,F,100,1.0D-5,1.0D-5,0.2D0,RCL,INA)
   GO TO (11,12,13,14),ITEST
11 CALL EVAL(X,F,AL,B,T)
   GO TO 10
12 WRITE(6,2) X,F,AL,B,T
   2 FORMAT(1H0,10X,'BEST VALUE OF A=',D15.5//,
   * 10X,' THE FUNCTIONAL AT THE MINIMUM IS =',D15.5//,
   * 10X,' THE SHAPE FACTR IS =',D15.5//,
   * 10X,'THE INTEGRAL WAS EVALUATED FRCM',D15.5,'TO',D15.5////)
   GO TO 1000
13 WRITE(6,3) F
   3 FORMAT(10X,' ERROR DUE TO ROUND OFF A=',D15.5,'F=',D15.5////)
   GO TO 1000
14 WRITE(6,4) F
   4 FORMAT(10X,'TCC MANY ITERATIONS A=',D15.5,'F=',D15.5////)
   GO TO 1000
900 STOP
END
SUBROUTINE EVAL(A,F,AL,B,T)
IMPLICIT REAL*8 (A-H,O-Z)
DIMENSION Z(7),W(8)
DATA Z/0.2C1194C93957435D0,0.3941E1347077563D0,
1 0.570972172608539D0,0.724417721360170D0,0.848206583410427D0,
2 0.937273392400706D0,0.987992518020485D0/

```

```
CATA W/0 .198431485327111D0,0.1E61E1C001155E2D0.
1 C.16E26S20E16554D0,0.139570677926154D0,0.107159220467172C0,
2 0.07G366047488108D0,0.03075324199E117D0, C.202578241925561C0/
SUM=0.0D0
C=(T-B)/2.0D0
C=(T+E)/2.0D0
SLM=SLM+*(S)*FUNCTN(D)
DO I I=1,7
Z1=C*Z(I)+C
Z2=C-C*Z(I)
1 SUM=SUM+W(I)*(FUNCTN(Z1)+FUNCTN(Z2))
F=C*SUM
RETURN
END
FUNCTION FUNCTN(Y)
IMPLICIT REAL*8 (A-H,O-Z)
COMMON X,AL
V1=V(1.0D0,AL,Y)
V2=V(X,1.0D0,Y)
FUNCTR=(1.0D0-V2/V1)**2
RETURN
END
END OF FILE ON SYSIN.
```

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```
C THIS PROGRAM EVALUATES THE INTEGRALS OF SITE-SIYE DIRECT
C CORRELATION INTEGRALS OF THE FORM PROPOSED BY LOWDEN AND CHANDLER
C IMPLICIT REAL*8 (A-H,O-Z)
C DIMENSION ALDS(30),RHOS(30),A11(30),A21(30),A31(30),A41(30),
C * A22(30),A32(30),A42(30),A23(30),A33(30),A43(30),A(30),T(15)
C N IS THE NUMBER OF STATE CONDITIONS EVALUATED
C READ(5,1) N
1 FORMAT(12)
 00 10 I = 1,N
10 READ(5,2)ALDS(I),RHOS(I)
2 FORMAT(2F10.4)
  I = 1
47 READ(5,3) A
3 FORMAT(8F10.4)
  GO TO (200,201,202,203,204,205,206,207,208,209),I
200 DC 100 J = 1,N
100 A11(J) = A(J)
  GC T5 19
201 DO 101 J = 1,N
101 A21(J) = A(J)
  GC T6 19
202 DC 102 J = 1,N
102 A31(J) = A(J)
  GC T7 19
203 DO 103 J = 1,N
103 A41(J) = A(J)
  GC T8 19
204 DC 104 J = 1,N
104 A22(J) = A(J)
  GO T9 19
205 DO 105 J = 1,N
105 A32(J) = A(J)
  GO T10 19
206 DC 106 J = 1,N
106 A42(J) = A(J)
  GO T11 19
207 DC 107 J = 1,N
107 A23(J) = A(J)
  GC T12 19
208 DC 108 J = 1,N
108 A33(J) = A(J)
  GO T13 19
209 DC 109 J = 1,N
109 A43(J) = A(J)
```

```

19 I = I + 1
  IF(I.EQ.11) GO TO 21
  GC TO 47
21 DO 30 I=1,n
  AL = ALDS(I)
  BE = 1.0D0 - AL
  T(1) = (A11(I)-A21(I)+A31(I)-A41(I))/3.0D0
  T(2) = (A21(I)-2.0D0*A31(I)+3.0D0*A41(I))/4.0D0
  T(3) = (A31(I)-3.0D0*A41(I))/5.0D0
  T(4) = A41(I)/6.0D0
  T(5)=(AL**3)*(0.0D0 -AL*A22(I)+(AL**2)*A32(I)-(AL**3)*A42(I))/3.0D0
  T(6)=(AL**4)*(A22(I)-2.0D0*AL*A32(I)+3.0D0*(AL**2)*A42(I))/4.0D0
  T(7)=(AL**5)*(A32(I)-3.0D0*AL*A42(I))/5.0D0
  T(8) =(AL**6)*A42(I)/6.0D0
  T(9)=BE**3*(C.0D0 -3E*A23(I)+(BE**2)*A33(I)-(BE**3)*A43(I))/3.0D0
  T(10)=BE**4*(A23(I)-2.0D0*BE*A33(I)+3.0D0*(BE**2)*A43(I))/4.0D0
  T(11)=BE**5*(A33(I)-3.0D0*BE*A43(I))/5.0D0
  T(12)=(BE**6)*A43(I)/6.0D0
  SUM = 0.0D0
  DO 40 J = 1,12
40 SUM = SUM + T(J)
  C = 16.0D0*3.141592*RHOS(I)*SUM
  AKD = 1.0DC - C
  WRITE(6,1000)C,AKD,ALDS(I),RHOS(I),SUM
1000 FORMAT(10X,' THE DCF INTEGRAL IS ',F15.4,//,
* 10X,' THE DIMENSIONLESS COMPRESSIBILITY IS ',F15.4,//,
* 10X,' L/S = ',F10.4,' AND RH0*SIG**3 = ',F10.4//,
* 20X,' THE INTEGRAL WAS ', F20.6)

```

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```

C      EXCESS ENTHALPY CALCULATIONS FROM UNIFAC
C      LIMITED TO FIVE MOLECULES WITH TEN GROUPS
DIMENSION XM(5),X(10),R(10),Q(10),A(10,10),ADT(10,10)
DIMENSION AEXP(10,10),ANU(10,5)
DIMENSION SUMX(10)
COMMON SUM
READ(5,123) NG,NM
123 FORMAT(2I11)
READ(5,124)(G(I),I=1,NG)
DO 100 I=1,NG
READ(5,124)(A(I,J),J=1,NG)
READ(5,124)(ANU(I,J),J=1,NM)
124 FORMAT(8F10.0)
100 CONTINUE
READ(5,*), T
CALL ATERMS(A,NG,ADT,AEXP,T)
DO 1 I=1,21
AIM=I-1
XM(1)=0.05*AIM
XM(2)=1.0-XM(1)
CALL GFRAC(XM,X,NG,NM,ANU)
CALL HEG(X,Q,ADT,AEXP,T,NG,HEXG)
CALL HEGR(XM,Q,ADT,AEXP,ANU,T,NM,NG,HEXR)
HEXGC=SUM#HEXG
HEX=HEXGC-HEXR
WRITE(6,10)(XM(I),I=1,NM)
10 FORMAT(10X,'MOLE FRACTIONS ---',20X,4(5X,F10.4))
WRITE(6,11)(X(I),I=1,NG)
11 FORMAT(10X,' GROUP FRACTIONS ---',20X,4(5X,F10.4))
WRITE(6,12) HEXGC,HEXR,HEX
12 FORMAT(10X,' GROUP CONTRIBUTION = ',F10.4,//
*,10X,' REFERENCE CONTRIBUTION = ',F10.4,//
*,10X,' EXCESS ENTHALPY = ',F10.5)
1 CONTINUE
STOP
END
SUBROUTINE ATERMS(A,NG,ADT,AEXP,T)
DIMENSION XM(5),X(10),R(10),Q(10),A(10,10),ADT(10,10)
DIMENSION AEXP(10,10),ANU(10,5)
DO 1 I=1,NG
DO 1 J=1,NG
ADT(I,J)=A(I,J)/T
1 AEXP(I,J)=EXP(-ADT(I,J))
RETURN

```

```
ENC
SUBROUTINE GFRAC(XM,X,NG,NM,ANU)
DIMENSION XM(5),X(10),R(10),Q(10),A(10,10),AOT(10,10)
DIMENSION AEXP(10,10),ANU(10,5)
DIMENSION SUMX(10)
COMMON SUM
SUM=0.0
DO 2 I=1,NG
SUMX(I)=0.0
DO 1 J=1,NM
1 SUMX(I) = SUMX(I) + XM(J)*ANU(I,J)
2 SUM = SUM + SUMX(I)
DO 3 I=1,NG
3 X(I) = SUMX(I)/SUM
RETURN
END
SUBROUTINE FEC(X,Q,A,T,N,HEX)
DIMENSION X(10),Q(10),A(10,10),AOT(10,10),AEXP(10,10)
DO 1 I=1,N
DO 1 J=1,N
AOT(I,J) = A(I,J)/T
1 AEXP(I,J) = EXP(-AOT(I,J))
SLMA=0.0
DO 2 K=1,N
SUMB=0.0
SLMC=0.0
DO 3 L=1,N
ACC = X(L)*C(L)*AEXP(L,K)

```

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```
SUM3=SUMB+ADD*ACT(L,K)
3 SUMC=SUMC+ACC
2 SLMA=SUMA+X(K)*Q(K)*SUMB/SUMC
HEXR=SUMA*8.E14*T
RETURN
END
SUBROUTINE HEGR(XM,Q,ADT,AEXP,ANU,T,NM,NG,HEXR)
DIMENSION XM(5),X(10),R(10),Q(10),A(10,10),ADT(10,10)
DIMENSION AEXP(10,10),ANU(10,5)
SUMM=0.0
DC 5 I=1,NM
SLMA=C.0
DC 2 K=1,NG
SLMB=0.0
SUMC=0.0
DC 3 L=1,NC
ACC=ANU(L,I)*C(L)*AEXP(L,K)
SUM3=SUMB+ADD*ADT(L,K)
3 SUMC=SUMC+ACC
2 SLMA=SUMA+ANU(K,I)*C(K)*SUME/SUMC
5 SUMM=SUMM+SLMA*XN(I)
HEXR=SLMM*8.314*T
RETURN
END

END CF FILE CN SYSIN.
```

APPENDIX 7
COMPRESSIBILITY THEOREM FROM RISM THEORY

The purpose of this appendix is to show that a general compressibility theorem exists for systems for which the RISM theory applies.

The starting point for this derivation is the constant temperature Gibbs-Duhem equation

$$dP\beta = \sum_i \rho_i d\beta \mu_i \quad (A7-1)$$

We wish to expand the differentials on the right-hand side of this equation as

$$dP\beta = \sum_{ij} \rho_i \left(\frac{\partial \beta \mu}{\partial \rho} \right)_{T, \rho_k \neq j} d\rho_j \quad (A7-2)$$

And then we must identify the partial derivatives of interest here. We do know that

$$\left(\frac{\partial \rho_i}{\partial \beta \mu_j} \right)_{T, \mu_k \neq j} = \rho_i [\delta_{ij} + \rho_j H_{ij}] \quad (A7-3)$$

And forming these elements into a matrix representation gives

$$\left(\frac{\partial \rho_i}{\partial \beta u_j}\right)_{T, \mu_{k \neq j}} = [\underline{\rho} + \underline{\rho} \underline{H} \underline{\rho}]_{ij} \quad (A7-4)$$

And then a thermodynamic identity gives

$$\left(\frac{\partial \beta u_i}{\partial \rho_j}\right)_{T, \rho_{k \neq j}} = \{[\underline{\rho} + \underline{\rho} \underline{H} \underline{\rho}]^{-1}\}_{ij} \quad (A7-5)$$

Note here that

$$\underline{\rho} + \underline{\rho} \underline{H} \underline{\rho} = [\underline{\underline{\rho}} + \underline{\rho} \underline{H}] \underline{\rho} \quad (A7-6a)$$

$$\therefore [\underline{\rho} + \underline{\rho} \underline{H} \underline{\rho}]^{-1} = \underline{\rho}^{-1} [\underline{\underline{\rho}} + \underline{\rho} \underline{H}]^{-1} \quad (A7-6b)$$

and the ij -th element is $\frac{1}{\rho_i} \{[\underline{\underline{\rho}} + \underline{\rho} \underline{H}]^{-1}\}_{ij}$

Thus

$$dP\beta = \sum_{ij} \{[\underline{\underline{\rho}} + \underline{\rho} \underline{H}]^{-1}\}_{ij} d\rho_j \quad (A7-7)$$

So now we must determine the term in brackets.

To do this, first note that

$$[\underline{\underline{\rho}} + \underline{\rho} \underline{H}]_{ij} = \delta_{ij} + \rho_i H_{ij} \quad (A7-8)$$

These terms must be related to the site-site correlation functions of the RISM theory. Here the nomenclature of Lombardero and Encisco (1981) is used. The multicomponent RISM equation is (in Fourier space)

$$\hat{h} = \hat{\omega}_C [I - \rho \hat{\chi}_C]^{-1} \hat{\omega} \quad (A7-9)$$

All of the terms here can be considered as either standard square matrices of dimensions

$$\sum_{\substack{\text{all} \\ \text{types} \\ \text{of} \\ \text{molecules}}} \text{number of sites in molecule } i$$

or simply as fourth order tensors. To explain the nomenclature

$h_{ij}^{\alpha\beta}$ = total correlation function between site α on a molecule of type i and site β on a molecule of type j .

There is of course an analogous nomenclature for the site-site direct correlation functions.

The $\hat{\omega}$ matrix has elements of the form

$$\hat{\omega}_{ij}^{\alpha\beta} = \delta_{ij} \hat{\omega}_j^{\alpha\beta} \quad (A7-10)$$

where $\hat{\omega}_j^{\alpha\beta}$ is the Fourier transform of the intramolecular correlation function for sites α and β on a molecule of type j . The $\hat{\chi}$ matrix has elements

$$\hat{x}_{ij}^{\alpha\beta} = x_j \delta_{ij} \hat{w}_j^{\alpha\beta} \quad (\text{A7-11})$$

We shall also require one other auxiliary matrix, σ , defined as

$$\sigma_{ij}^{\alpha\beta} = \delta_{ij} \delta_{\alpha\beta} \rho_i \quad (\text{A7-12})$$

Now consider

$$\left[\hat{\omega} + \frac{\sigma h}{\rho} \right]_{ij}^{\alpha\beta} = \hat{\omega}_{ij}^{\alpha\beta} + \rho_i \hat{h}_{ij}^{\alpha\beta} \quad (\text{A7-13})$$

This matrix is of interest because (Chandler and Richardson, 1984)

$$\lim_{k \rightarrow \infty} \left[\hat{\omega} + \frac{\sigma h}{\rho} \right]_{ij}^{\alpha\beta} = \delta_{ij} + \rho_i H_{ij} \quad (\text{A7-14})$$

And these are the terms required to construct the compressibility relation. We now wish to relate these to the site-site direct correlation functions. This is shown below.

Using the RISM equation we have

$$\hat{\omega} + \frac{\hat{\sigma} \hat{h}}{\rho} = \left\{ I + \frac{\hat{\sigma} \hat{w} \hat{C}}{\rho} [I - \rho \hat{w} \hat{C}]^{-1} \right\} \hat{w} \quad (\text{A7-15})$$

And this leads to

$$\hat{\underline{I}}_{\approx} + \hat{\underline{\sigma h}}_{\approx\approx}^{-1} = [\hat{\underline{I}}_{\approx} - \hat{\underline{\rho Xc}}_{\approx\approx} + \hat{\underline{\sigma wc}}_{\approx\approx}] [\hat{\underline{I}}_{\approx} - \hat{\underline{\rho Xc}}_{\approx\approx}]^{-1} \quad (\text{A7-16})$$

However, a simple computation will show that

$$\hat{\underline{\sigma \omega}}_{\approx\approx} = \hat{\underline{\rho X}}_{\approx\approx} \quad (\text{A7-17})$$

And thus

$$\hat{\underline{\omega}}_{\approx} + \hat{\underline{\sigma h}}_{\approx\approx} = [\hat{\underline{I}}_{\approx} - \hat{\underline{\rho Xc}}_{\approx\approx}]^{-1} \hat{\underline{\omega}}_{\approx} \quad (\text{A7-18})$$

$$\text{Let } \hat{\underline{M}}_{\approx} = [\hat{\underline{I}}_{\approx} - \hat{\underline{\rho Xc}}_{\approx\approx}]^{-1} \quad (\text{A7-19})$$

Then we can show

$$\lim_{k \rightarrow \infty} \{\hat{\underline{\omega}}_{\approx} + \hat{\underline{\sigma h}}_{\approx\approx}\}_{ij}^{\alpha\beta} = \sum_{\beta} \hat{M}_{ij}^{\alpha\beta}(\infty) \equiv M_{ij}^{\alpha} = (\underline{M}_{\infty}^{\alpha})_{ij} \quad (\text{A7-20})$$

And thus we have

$$dP^{\beta} = \sum_{ij} [(\underline{M}^{\alpha})^{-1}]_{ij} d\rho_j \quad (\text{A7-21})$$

We then wish to determine \underline{M}^{α} and its inverse. From the definition of the matrix inverse we know that

$$\hat{\underline{I}}_{\approx} = \hat{\underline{MM}}_{\approx\approx}^{-1} \quad (\text{A7-22a})$$

or in component notation

$$\delta_{ij}\delta_{\alpha\beta} = \sum_{\ell\gamma} \hat{M}_{i\ell}^{\alpha\gamma} (\hat{M}_z^{-1})_{\ell j}^{\gamma\beta} \quad (A7-22b)$$

$$\text{But } \hat{M}_z^{-1} = I_z - \rho \hat{X}_z \hat{C}_z \quad (A7-23)$$

$$\text{Thus } (\hat{M}_z^{-1})_{\ell j}^{\gamma\beta} = \delta_{\ell j} \delta_{\gamma\beta} - \rho \sum_{\delta} X_{\ell} \hat{\omega}_{\ell}^{\gamma\delta} \hat{C}_{\ell j}^{\delta\beta} \quad (A7-24)$$

Then we have

$$\delta_{ij}\delta_{\alpha\beta} = \sum_{\ell\gamma} \hat{M}_{i\ell}^{\alpha\beta} \left\{ \delta_{\ell j} \delta_{\gamma\beta} - \rho \sum_{\delta} X_{\ell} \hat{\omega}_{\ell}^{\gamma\delta} \hat{C}_{\ell}^{\alpha\beta} \right\} \quad (A7-25a)$$

$$= \hat{M}_{ij}^{\alpha\beta} - \rho \sum_{\ell\gamma\delta} X_{\ell} \hat{M}_{i\ell}^{\alpha\beta} \hat{\omega}_{\ell}^{\gamma\delta} \hat{C}_{\ell j}^{\alpha\beta} \quad (A7-25b)$$

And in the long wavelength limit this is

$$\delta_{ij}\delta_{\alpha\beta} = M_{ij}^{\alpha\beta}(o) - \rho \sum_{\ell\gamma\delta} X_{\ell} M_{i\ell}^{\alpha\beta}(o) \hat{C}_{\ell j}^{\delta\beta}(o) \quad (A7-26)$$

If this expression is the summed over β we find

$$\delta_{ij} = M_{ij}^{\alpha} - \rho \sum_{\ell} X_{\ell} M_{i\ell}^{\alpha} \sum_{\delta\beta} \hat{C}_{\ell j}^{\alpha\beta}(o) \quad (A7-27)$$

$$\text{Define } C_{\ell j} = \sum_{\delta\beta} \hat{C}_{\ell j}^{\delta\beta}(o) \quad (A7-28)$$

Then in matrix form this is

$$\underline{\underline{I}} = \underline{\underline{M}}^{\alpha} - \underline{\underline{M}}^{\alpha} \underline{\underline{\rho}} \underline{\underline{C}} \quad (A7-29)$$

$$\text{And therefore } \underline{\underline{M}}^{\alpha} = (\underline{\underline{I}} - \rho \underline{\underline{C}})^{-1} \quad (\text{A7-30})$$

$$\text{and then } (\underline{\underline{M}}^{\alpha})^{-1} = \underline{\underline{I}} - \rho \underline{\underline{C}} \quad (\text{A7-31})$$

This then leads to

$$dP\beta = \sum_{ij} (\delta_{ij} - \rho_i c_{ij}) d\rho_j \quad (\text{A7-32})$$

And we then have the compressibility theorem

$$\left(\frac{\partial P\beta}{\partial \rho} \right)_{T, \underline{\underline{X}}} = \sum_{ij} x_j (\delta_{ij} - \rho_i c_{ij}) \quad (\text{A7-33})$$

This is exactly the same as the molecular form if one makes the identification

$$c_{ij} = \sum_{\alpha\beta} c_{ij}^{\alpha\beta} \quad (\text{A7-34})$$

which has been used throughout this work. It should be noted here that this derivation requires only the evaluation of the sum of site-site functions in the $k \rightarrow 0$ limit which is believed to always be well bounded.

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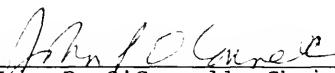
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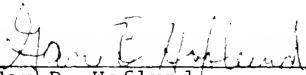
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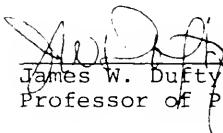
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Gar B. Hoflund
Professor of Chemical Engineering

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and was accepted as partial fulfillment of the requirements
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